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Polymers as Advanced Materials for Desiccant Applications:

Progress Report for 1989

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PREFACE

In keeping with the national energy policy goal of fostering an adequate supply of energy at a reasonable cost, the U.S. Department of Energy (DOE) supports a variety of programs to promote a balanced and mixed energy resource system. The mission of the DOE Solar Building Research and Development Program is to support this goal by providing for the development of solar technology alternatives for the buildings sector. It is the goal of the program to establish a proven technology base to allow industry to develop solar products and designs for buildings that are economically competitive and can contribute significantly to building energy supplies nationally. Toward this end, the program sponsors research activities related to increasing the efficiency, reducing the cost, and improving the long-term durability of passive and active solar systems for building water and space heating, cooling, and daylighting applications. These activities are conducted in four major areas: (1) Advanced Passive Solar Materials Research, (2) Collector Technology Research, (3) Cooling Systems Research, and (4) Systems Analysis and Applications Research.

Advanced Passive Solar Materials Research. This activity area includes work on new aperture materials for controlling solar heat gains and enhancing the use of daylight for building interior lighting purposes. It also encompasses work on low-cost thermal storage materials that have high thermal storage capacity and can be integrated with conventional building elements and work on materials and methods to transport thermal energy efficiently between any building exterior surface and the building interior by nonmechanical means.

Collector Technology Research. This activity area encompasses work on advanced low- to medium-temperature (as high as 180°F useful operating temperature) flat-plate collectors for water and space heating applications, and medium- to high-temperature (as high as 400°F useful operating temperature) evacuated-tube concentrating collectors for space heating and cooling applications. The focus is on design innovations using new materials and fabrication techniques.

Cooling Systems Research. This activity area involves research on high-performance dehumidifiers and chillers that can operate efficiently with the variable thermal output and delivery temperatures associated with solar collectors. It also includes work on advanced passive cooling techniques.

Systems Analysis and Applications Research. This activity area encompasses experimental testing, analysis, and evaluation for solar heating, cooling, and daylighting systems for residential and nonresidential buildings. This involves system integration studies; the development of design and analysis tools; and the establishment of overall cost, performance, and durability targets for various technology or system options.

This work relates to Cooling Systems Research for improving the performance of desiccant cooling systems (DCSs) that process water vapor in an atmosphere to produce cooling. By identifying a next-generation, low-cost, advanced desiccant material, the cost of air conditioning buildings can be lowered by improving the performance of DCSs and eliminating the need to add peak-load electric generating capacity.

This report documents the work accomplished during calendar year 1989 as a continuation of a subtask begun in 1985 in the Solar Desiccant Cooling Program. The work was carried out by H. H. Neidlinger, Y. Shinton, R. Goggin, and A. W. Czanderna. The author emphasizes that this is a progress report on the advanced desiccant materials research subtask and, therefore, includes material not normally presented in a technical report.

AW Czanderna

A. W. Czanderna, Subtask Leader

SUMMARY

The technological objective of this work is to identify a next-generation, low-cost material with which solar energy or heat from another low-cost energy source can be used for regenerating the water vapor sorption activity of the desiccant. The scientific objective of this task is to determine how the desired sorption performance of advanced desiccant materials (ADMs) can be predicted by understanding the role of the materials modifications and their surface phenomena.

This research is concerned with solid materials used as desiccants for desiccant cooling systems (DCSs) that process water vapor in an atmosphere to produce cooling. The purpose of the Advanced Desiccant Materials project during 1989 was to prepare ionic salts of polystyrene sulfonic acid (PSSA), synthesize a new desiccant polymer, and evaluate the sorption performance of these and similar commercially available polymeric materials for their potential application in solid commercial DCSs (CDCSs). An ADM can advance solar buildings technology not only by lowering the cost of solar-regenerated CDCSs to compete with conventional air conditioning but also by eliminating the need for adding peak-load generating capacity by electric utilities.

Background information is presented that includes an introduction to DCSs and the role of the desiccant as a system component. The purpose, background, rationale, and long-term technical approach for studying ADMs are reported, including using polymers as ADMs and the key research issues concerning polymers. The experimental method for measuring water vapor sorption by desiccants is described for a quartz crystal microbalance (QCM).

The water vapor sorption performance criteria used for screening the modified polymers prepared this year include the water sorption capacity from 5% to 80% relative humidity (R.H.), isotherm shape, and rate of adsorption and desorption. These criteria are in addition to the key materials parameters for ranking potential ADMs, which are listed from a previous report. Because the isotherm shape is especially important, based on work by others, the discussion of our results focuses considerable attention on improving isotherms from the linear behavior obtained for silica gel to a Type 1M behavior. The procedures used for preparing the polymers for studies with the QCM are discussed in general and are given specifically for the different types of polymers prepared.

Measurements are presented for the sorption performance of modified polymeric ADM materials with the QCM. The data include sorption isotherms and adsorption and desorption kinetics. Alkali ion salts of PSSA, which are commercially available, were used for our polymer modification studies. From sorption capacity measurements of the alkali ion salts of PSSA, it was demonstrated that the isotherm shape depends on the cation (counterion) present. The best isotherm shape and capacity are obtained for PSSA and PSSA lithium salt (PSSALS), but the optimum preparation scheme has not been deduced. The other salts studied were sodium salt (PSSASS) and potassium salt (PSSAKS).

Isotherms of PSSA taken over a 5-month period show that the material has a dramatic loss in capacity and that the isotherm shape is time dependent. The cause for these changes is not known. Isotherms of PSSA retained in a dichloroethane solution have unfavorable shapes or capacities. In order of

decreasing suitability for CDCSs, the shape and capacity of isotherms for PSSA > PSSALS ≃ PSSASS > PSSAKS and are inversely related to the cation size. However, the changes in PSSA preclude it from candidate status at this time. Wide variations in the sorption capacity for different formulations (sources) of PSSASS were observed, where only the best material is comparable to an off-the-shelf PSSALS. PSSA ammonium salt (PSSAAS) exhibits a large hysteresis between adsorption and desorption and so is unsuitable for CDCS applications. Isotherms obtained at 17°, 22.1°, and 27°C using PSSA, PSSALS, PSSASS, and sodium polystyrene sulfonate (SPSS, a special 90% sulfonated form of PSSASS) exhibit an unexpected maximum at 22.1°C. Cellulose sulfate sodium salt (CSSS) isotherms were also determined from another commercial supplier and found to have more capacity (13% at 60% R.H.) than the prior supplier (10% at 60% R.H.) while retaining the favorable Type 2 isotherm shape and cyclic stability previously observed.

The adsorption and desorption kinetics for PSSA and all the ionic salts of it studied (PSSALS, PSSASS, PSSAKS, and PSSAAS) are easily fast enough for CDCS applications with a wheel rotation speed of 6 min per revolution. More than 90% of the capacity change during adsorption and desorption at 22.1°C occurs within a total of 3 min. For CSSS, even more favorable kinetics are observed where the comparable total time is only 2 min, and this is only slightly dependent with temperature for data taken at 17°, 22.1°, and 27°C. No significant differences in sorption rates of PSSASS and CSSS could be detected for thicknesses ranging between 1 and 10 μm. Thicker samples have not been successfully studied with the QCM.

A new data-acquisition system (DAQS) was used to collect and store data and to display it in many flexible ways. Examples that are especially relevant are presented.

A Sartorius beam microbalance system for measuring water vapor sorption was installed and may be used in 1990 to characterize the modified or synthesized desiccant polymers. The QCM data collection, storage, and retrieval system has been used to study the kinetics of adsorption and desorption and assess the possibility of making water diffusivity measurements while maintaining its outstanding capability for characterizing the water sorption performance parameters of polymeric ADMs.

Future activities for the project are addressed. The priority need for continuing to modify existing polymers or "molecularly engineering" the preparation of polymers to serve as an ideal desiccant is highlighted. Characterization of polymers prepared by Eastman Kodak will be the entire task activity for FY 1990.

A 5-year summary of the project and a recent publication in the ASHRAE proceedings are included as Appendix A and Appendix I, respectively. The reader may find it helpful to read Appendix A and then Appendix I before plunging into the detail of the entire report.

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ACRONYMS

ADM	advanced desiccant material
BET	Brunauer, Emmett, and Teller (isotherm classifications)
CDCS	commercial desiccant cooling system
CFM	cubic feet per minute
COP	coefficient of performance
CSSS	cellulose sulfate sodium salt
DAQS	data-acquisition system
DCS	desiccant cooling system
DOE	Department of Energy
GPC	gel permeation chromotography
GRI	Gas Research Institute
HVAC	heating, ventilating, and air conditioning
MC	methyl cellulose
MW	molecular weight
PACM	polyacrylamide-carboxyl modified
PMAASS	poly(methacrylic acid) sodium salt
PS	polystyrene
PSSA	polystyrene sulfonic acid
PSSAAS	polystyrene sulfonic acid ammonium salt
PSSAKS	polystyrene sulfonic acid potassium salt
PSSALS	polystyrene sulfonic acid lithium salt
PSSASS	polystyrene sulfonic acid sodium salt
PV	photovoltaics
PVAVSSS	poly(n-vinylacetamide, vinyl sulfonate) sodium salt
QC	quartz crystal
QCM	quartz crystal microbalance
R.H.	relative humidity
SEM	scanning electron microscopy
SERI	Solar Energy Research Institute
SPSS	sodium polystyrene sulfonate

1.0 INTRODUCTION

1.1 Objectives and Previous Reports

1.1.1 Objectives

The technological objective of this work is to identify a next-generation, low-cost material with which solar energy or heat from another low-cost energy source can be used for regenerating the water vapor sorption activity of the desiccant.

The scientific objective is to determine how the desired sorption performance of advanced desiccant materials (ADMs) can be predicted by understanding the role of the materials modifications and their surface phenomena.

1.1.2 Previous Reports

Because many readers might not have a complete set of prior reports for the years 1985-1988, the information they need to know from those reports is integrated into this report, either directly in the main body of the report or into an appendix. Where detail about other aspects of the previous work (e.g., experimental apparatus, design, and construction) is not crucial to understanding the results and discussion of the progress made in calendar year 1989, which is the subject of this report, the reader is referred to the appropriate documents.

1.2 Background

This research is concerned with solid materials used as desiccants for desiccant cooling systems (DCSs) that process water vapor in an atmosphere to produce net cooling. Because mass transfer occurs between the system and its environment, these systems are commonly referred to as open-cycle systems (Collier, Barlow, and Arnold 1982). All these systems use a liquid or solid material called a desiccant to remove water vapor from the air either by adsorption onto or into a solid desiccant or by absorption into the liquid desiccants. This report focuses on polymeric materials for use in the solid-type desiccant systems, although the reader will recognize the possible opportunities for use in liquid-based systems. A discussion about DCSs is given in Appendix B.1.

Commercial solar-regenerated DCSs must compete with vapor compression as well as all other space cooling technologies, so electrical and thermal coefficients of performance (COPs) and initial capital costs are primary concerns. From thermodynamic analyses of desiccant cooling cycles, it is apparent that the adsorption characteristics of the desiccant can have a large influence on the cooling capacity and COP of the cycle (Collier, Barlow, and Arnold 1982; Jurinak 1982). This effect was quantified in a recent computer parametric systems analysis study (Collier, Cale, and Lavan 1986). Although this study assumed a regeneration temperature of 160°C, the conclusions about an "ideal" desiccant are also applicable for solar regeneration temperatures of 60° to 95°C. They concluded that if an "ideal" desiccant can be identified, the thermal COP of a DCS can be improved from 0.85 to 1.05, which can now be obtained with silica gel, to a minimum of 1.3 to 1.4 or closer to the theoretical maximum of about 2.5. (Ideal is in quotes because there are properties of an ideal desiccant that were not included in his study. Isotherm shapes are discussed below and are important for our work.) At the same time, the cubic feet per minute (cfm) per ton can be reduced from a range of 310 to 400 for silica gel to a range of 200 to 250 for an "ideal" desiccant. The reduction in cfm/ton must not be overlooked because this factor can reduce the physical size of commercial DCSs and keep electrical parasitic consumption low. If both these factors were achieved, DCSs could be cost competitive with other current air conditioning systems; this is not possible for silica gel (Collier, Cale, and Lavan 1986).

For the computer parametric analysis, Collier, Cale, and Lavan (1986) chose five types of isotherms that they designated as Brunauer Type 1 extreme, Type 1 moderate, linear, Type 3 moderate, and Type 3 extreme. In Figure 1-1, we redrew the Type 1 moderate, Brunauer, Emmett, and Teller (BET) Type 2, Type 3 moderate, and linear isotherms used for the study. The Type 1 moderate isotherm is the optimum shape for the "ideal" desiccant, and the sorption should follow this isotherm between 5% and 60% relative humidity (R.H.) for best results (Collier 1987). We also plotted the isotherm for a silica gel, where the 37% water uptake at 100% R.H. is normalized to a loading fraction of 1.0, and part of the isotherm for polystyrene sulfonic acid sodium salt (PSSASS), where the 40% water uptake at 60% R.H. is normalized to a loading fraction of 1.0. As is seen, PSSASS is close to the Type 1 moderate isotherm shape as normalized, which is part of the reason we chose to emphasize modification of this polymer. At low R.H. of water vapor, the BET Type 2 isotherm has a knee that becomes more pronounced as the BET c value increases (Adamson 1990) from 50 to 200 or more. Larger c values correspond to increasing interactions between the gas and the solid. With c values below 10 (weaker interactions), the isotherms become linear and then Type 3 (moderate and then extreme). Thus, an objective of modifying polymers with Type 2 behavior is to increase the water vapor solid interactions to sharpen the knee (Adamson 1990) to track the Type 1 moderate shape. Interactions that are too strong produce a Type 1 extreme isotherm, which has nearly all its uptake or loading at a low R.H. Desiccants with Type 1 extreme isotherms are more difficult to regenerate, which is why the Type 1 moderate isotherm is favored (Collier, Cale, and Lavan 1986).

1.3 Purpose of ADMs Research

One purpose for performing long-range research on materials is to secure an understanding of the behavior of low-cost, high-performance next-generation technological materials, with a goal of extending the lifetime of these materials, or to identify new materials that will offer new options for components used in operating systems. The cost-effective deployment of DCSs is currently limited by the sorption performance, durability, and life-cycle cost of the inorganic materials used. Long-term materials research is needed that focuses on improving the properties of ADMs and identifying the reasons for degradation of their sorption performance.

The purpose of ADM R&D is to provide new materials options for DCS. The ultimate purpose is to identify materials with optimal performance in the temperature range used in a DCS in which the sorption activity of the desiccant can be routinely regenerated with an appropriate energy source. The performance of these materials can be ranked similarly to the performance of silica gel,

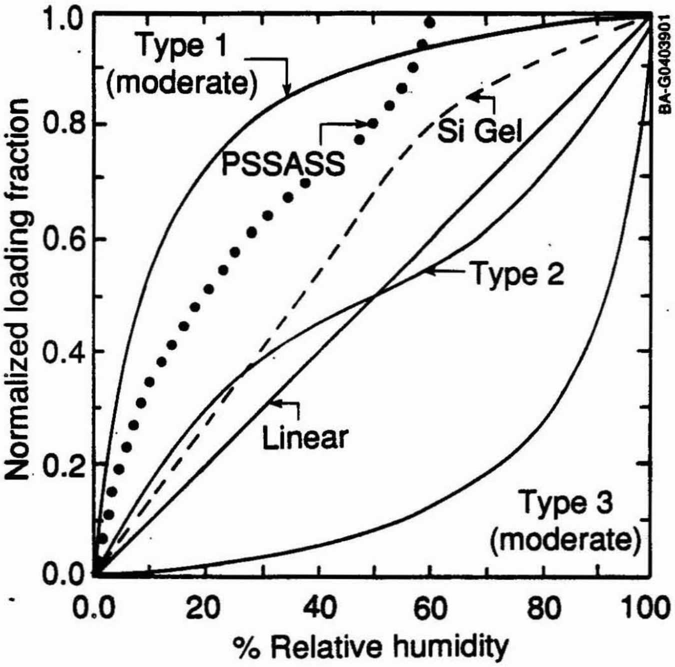


Figure 1-1. **Comparison of PSSASS and silica gel isotherms with Brunauer's and Collier's Type 1 moderate, Type 2, linear, and Type 3 moderate isotherms.**

which can be used as the standard for comparison. The life-cycle cost (i.e., initial cost, performance, and durability) has a direct relationship to the cost-effective deployment of any regenerative DCS. The identification of materials with extended lifetimes, enhanced reliability, and sustained desirable sorption properties for use in DCSs can be anticipated from a sustained R&D effort. Thus, an ADM can advance solar buildings technology not only by lowering the cost of commercial DCSs (CDCSs) to compete with conventional air conditioning but also by eliminating the need for electric utilities to add peak-load generating capacity. The relationship between desiccant materials and DCS and background information about ADM studies are discussed in Appendix B.2.

1.4 Polymers as ADMs

Polymers can serve as ADMs as discussed in Appendix B.3, which includes a listing of their potential benefits and identifies key research issues. Background for using solids to desiccate water vapor is given in Appendix B.4. Polymers must satisfy the same general criteria as any desiccant (Appendix C).

Our work for the past 5 years has involved the use of a rapid quartz crystal microbalance (QCM) method for evaluating the performance properties of ADMs, with an emphasis on polymers. These properties include water vapor sorption isotherms, adsorption and desorption kinetics, and cyclic stability. From past studies, we narrowed about 30 potentially viable, commercially available polymers to seven serious candidates for further study or modification. These are

o Polystyrene sulfonic acid sodium salt	(PSSASS)
o Polyacrylic acid ammonium salt	(PAAAS)
o Poly(methacrylic acid) sodium salt	(PMAASS)
o Poly(n-vinylacetamide, vinyl sulfonate) sodium salt	(PVAVSSS)
o Polyacrylic acid sodium salt	(PAASS)
o Cellulose sulfate sodium salt	(CSSS)
o Methyl cellulose	(MC).

During 1988, our efforts focused on modifying PSSASS and using commercial formulations of sodium polystyrene sulfonate (SPSS) with widely varying molecular weights (MWs). Both of these polymers are structurally the same as was discussed in Czanderna and Neidlinger (1990). During 1989, our focus was on studying various cationic salts of polystyrene sulfonic acid (PSSA). Eventually, those polymers with the best properties will be subjected to simulated use conditions, and cause for any performance losses will be identified. We also removed polyacryamide carboxyl modified from our candidate list of eight because of redefined criteria (Appendix C).

1.5 Summary of Progress from 1985 to 1989: Technical Approach

The long-term technical approach is summarized in Appendix D and was formulated to address the key technical issues listed in Appendix B.3. The sequence of the research, which has followed the technical approach, has been to perform a literature search of the sorption properties of candidate materials (Czanderna and Thomas 1986) and to carry out the experimental work.

The specific objectives of this multiyear task are (1) to determine the feasibility for using polymeric materials and chemically modified candidate materials as desiccants; (2) to determine the effect of chemically or physically modified desiccant surfaces on the sorption capacity, the heat of sorption, and the sorption kinetics; (3) to determine if fundamental water vapor-solid interactions limit the stability of naturally occurring and chemically modified candidate desiccant materials; and (4) to study the topographical and compositional changes at or near the water vapor-solid interface of desiccant materials resulting from adsorption-desorption cycles between 25°C and a higher temperature. When the objectives are met, there will be a sufficient understanding of the phenomena that are important to improving the performance, selecting materials, and extending the durability of DCS materials. The research will also provide mechanistic insights into the molecular processes that underpin the potential for predictive lifetime behavior of desiccant beds used in DCSs. For the latter, polymeric solids were chosen for our initial work because of their applications potential and remain as our primary focus.

Two principal activities were addressed during 1985: (1) identification of candidate materials for study and (2) construction of a QCM sorption apparatus. For the first activity, we completed a literature search, identified polymeric and inorganic materials as potential advanced desiccants, conducted a critical analysis of the literature, and ranked the materials for study. We also developed in detail the opportunities for using polymeric materials as ADMs. We identified the key materials parameters for ranking potential ADMs, and ranked all identified materials (more than 300 possibilities).

For the second activity, we first identified microgravimetric, compositional surface analytic, infrared spectroscopic, scanning electron microscopic, and thermal gravimetric measurements as the minimum number of techniques necessary for studying desiccant materials and understanding their morphological and surface properties. Then, we designed, purchased, assembled, constructed, installed, and initiated the use of a QCM for characterizing the sorption performance of organic (polymeric) and inorganic materials.

The results of the effort to identify the candidate materials and describe the QCM were fully documented (Czanderna and Thomas 1986, Section 2.0). This same report (Section 3.0) also included the results of the second activity.

During 1986, we concentrated on two activities: (1) to improve the operation of the QCM that was assembled in 1985, with an ultimate goal of having a fully automatic data collection of sorption isotherms and kinetics and (2) to obtain data on several of the 21 potential candidate polymers to initiate our process of narrowing these to candidate status. For the first activity, we achieved an acceptable level of semiautomatic operation of the QCM but could not obtain complete automation because of funding limitations. For the second activity, we obtained data on three polymers with widely varying sorption capacities. The details for both activities were summarized in Czanderna and Thomas (1987a, 1987b). In a related task at SERI, we demonstrated that surface compositional analysis using x-ray photoelectron spectroscopy and infrared spectroscopy will be useful for securing both fundamental and technological information about both present and advanced desiccant materials (Pesaran et al. 1986).

During 1987, we concentrated nearly all our effort on measuring the sorption performance of more than 23 potential candidate, commercially available, polymeric ADMs with the QCM. The measurements include sorption isotherms, rate of adsorption and desorption at each pressure increment or decrement, cyclic stability, and qualitative evaluations of permeation rates. We also identified the water vapor sorption performance criteria (Appendix C) for narrowing the potential ADM to a few candidate ADMs, where the sorption performance includes the sorption capacity from 5% to 80% R.H., isotherm shape, rate of adsorption and desorption, and cyclic stability of the ADM in water vapor. We used the criteria to narrow the number of polymeric materials to nine candidate ADMs. In addition, we designed a Sartorius microbalance system for use on the project as well as an experimental procedure for an existing thermal gravimetric apparatus for studying the cyclic stability of ADMs in humid air. We also initiated cyclic stability studies of several candidate polymeric ADM and established that eight polymers remain as serious candidate ADMs.

During 1988, a publication (Czanderna 1988) and a patent application were completed; these detail all prior work on this task. PSSASS and SPSS, both of which are commercially available, were used for our polymer modification studies. The SPSS studied to date has a narrower MW distribution than the PSSASS. From sorption capacity measurements of PSSASS and SPSS with different

MWs, it was demonstrated that the isotherm shape depends on the MW. More favorable isotherm shapes are obtained for MWs between 5000 and 66,100, but the optimum MW has not been deduced. Outside this MW region, the isotherms become more linear below 60% R.H. Accordingly, the first modification was to prepare PSSA by using polystyrene (PS) with MWs of 6000 and 50,000, which are available commercially. The second modification was to sulfonate the PS to the acid form, i.e., PSSA, and exchange the acid form with sodium ions to form PSSASS. The PSSAs were prepared with targeted sulfonic acid percentages of 20%, 40%, 60%, and 80%, which were then exchanged to form the corresponding PSSASS. The preliminary sorption data on these PSSASSs, indicate improved isotherms are obtained between 40% and 80% sulfonation; so, again, there is sensitivity to the polymer synthesis method. The commercially available SPSS is 90% sulfonated. Further work is required to establish if the optimum isotherm shape can be obtained within these sulfonation percentages. A third modification was initiated in which PSSA was exchanged with lithium ions. Furthermore, four cross-linked hydrogel polymers were synthesized. These are swelling polymers with the potential of sorbing water in excess of 10,000% of their own mass. If a swelling polymer can be successfully used in an engineering configuration, the large-capacity uptake will be especially attractive if it also produces an optimum isotherm shape. A Sartorius microbalance system for measuring water vapor sorption was installed and will also be used to characterize the modified or synthesized desiccant polymers when it becomes operable. The QCM data-collection, storage, and retrieval system was improved to permit studying adsorption and desorption kinetics to the limits of the quartz crystal (QC) controller and yet allow it to maintain its outstanding capability for characterizing the water sorption performance parameters of polymeric ADMs. In collaboration with the other SERI tasks, an initial calculation of the diffusivity was made for results on one polymer.

2.0 EXPERIMENTAL MEASUREMENT OF WATER VAPOR SORPTION BY POLYMERS

2.1 Introduction

The experimental apparatus for measuring the water vapor sorption by a solid is conceptually simple. An arrangement is needed where a solid can be surrounded by pure water vapor (or a partial pressure of water in the ambient atmosphere), and the number of water molecules that bond to the solid can be measured. A vacuum system can be used to control the gas (vapor) pressure over the solid. There are three basic methods for directly measuring the rate of gas adsorption and the equilibrium amount of vapor adsorbed by a solid: (1) gravimetric, (2) volumetric, and (3) radiotracer. The last is excluded because it would require tritiated water and offers no obvious advantages over gravimetric techniques. Gravimetric techniques have many advantages over volumetric techniques (Gregg and Sing 1982; Czanderna and Wolsky 1980), especially for water vapor sorption studies. Water is one of the most difficult vapors to work with for analysis when using vacuum systems, but the determination of adsorption isotherms and the rate of adsorption and desorption of water can be carried out routinely with gravimetric techniques.

2.2 QCM Apparatus

Of the available gravimetric techniques, the beam balance and the QCM are the two best choices when the advantages and limitations of all microbalances are considered (Czanderna and Wolsky 1980). We chose to use a QCM for our initial studies because of the commercial availability of QCMs and their ease of use for studying the sorption of water by materials at or near 25°C (Lu and Czanderna 1984). The experimental system, which is shown schematically in Figure 2-1, consists of a vacuum system, a residual gas analyzer, a QCM system with five QC sensors, and a temperature bath for the QCM. These components

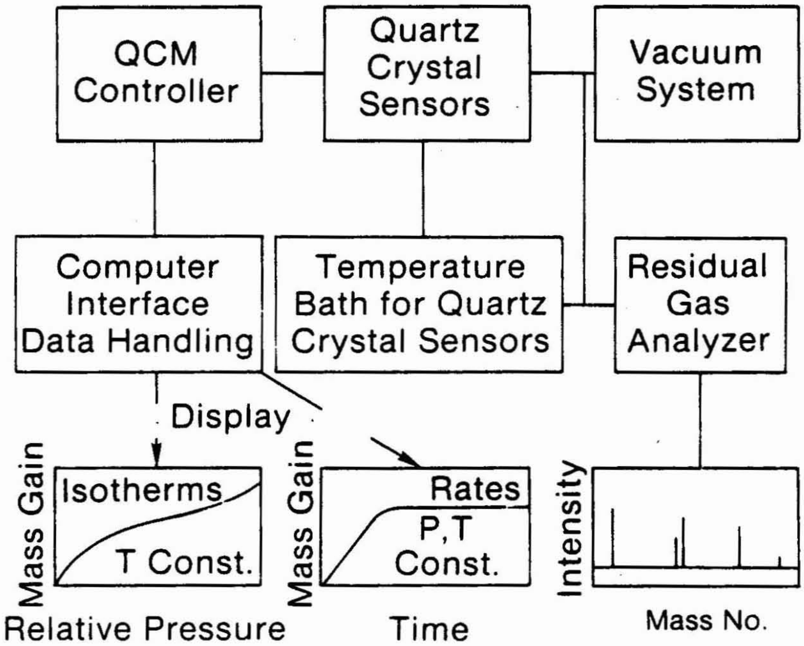


Figure 2-1. Block diagram showing the principal components of a quartz crystal microbalance apparatus

and their operation were described in detail in Czanderna and Thomas (1986) and are summarized in Appendix E.

During 1988, a new data-acquisition system (DAQS) was acquired to replace the obsolete MacSym 2 computer and printer originally used to obtain the mass data from the QCM and the temperature and pressure data. The hardware consists of an IBM compatible 80286 computer system with appropriate monitors, cards, internal RAM, disks, and acquisition components. The software enables the necessary functions to be accomplished for displaying, printing, and processing the data. The DAQS reads, stores, and plots the data for visual observation from the five QCs in the QCM system every 2 s as well as the pressure, bath temperature, room temperature, and temperature of two of the crystal holders. Results obtained using the DAQS are given in Section 4.6 and demonstrate some of the capabilities of the combined QC, QC controller, and DAQS.

For isotherm measurements, the polymers are mounted onto QCs as detailed in Czanderna (1988, Section 4.2). After determining the polymer mass, the QCs are mounted onto a QC holder. For the vacuum measurements, the QC holder is an integral part of a vacuum system apparatus, as shown in Figure 2-2. The essential components of this holder include a 2.75-in. stainless steel Conflat® vacuum flange, with feedthroughs for a thermocouple, cooling water, and the electrical leads needed for operating the oscillator. The essential components of the vacuum system include a source of pure water vapor, capacitance manometer, valves for manipulating gas pressures, pumps, and low-pressure gauges. Sample temperatures are measured with thermocouples. Detailed descriptions of the QCM and vacuum chamber components are available (Czanderna and Thomas 1986).

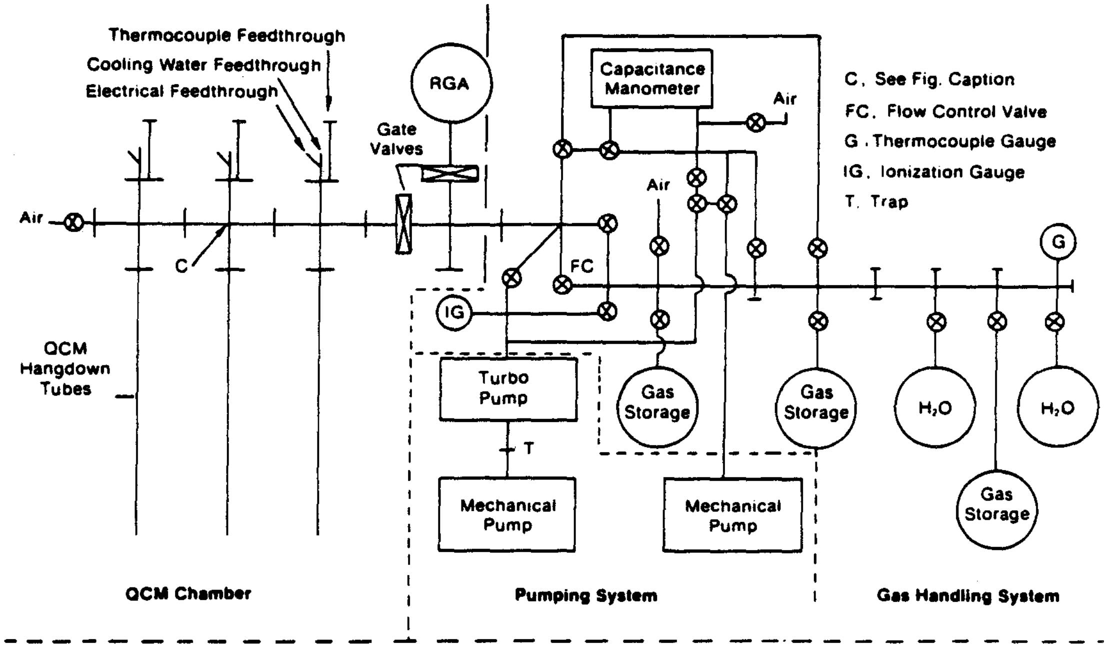


Figure 2-2. Schematic of vacuum system for QCM apparatus

2.3 Procedures Used for Determining Isotherms

For studying the polymers prepared in 1989, isotherms were normally determined at 22.1°C in pure water vapor using the QCM. The procedure, which is described in Appendix F, was also followed for isotherms measured at 17° and 27°C. The polymer-coated QC was mounted on the crystal holder and evacuated to $< 10^{-7}$ torr, which was usually 2×10^{-8} torr, until constant mass readings were observed. The mass lost during evacuation is used to correct the sample mass measured prior to evacuation. Water vapor was admitted or evacuated to the desired pressures using the gas handling and pumping system.

2.4 Kinetic and Cyclic Stability Studies

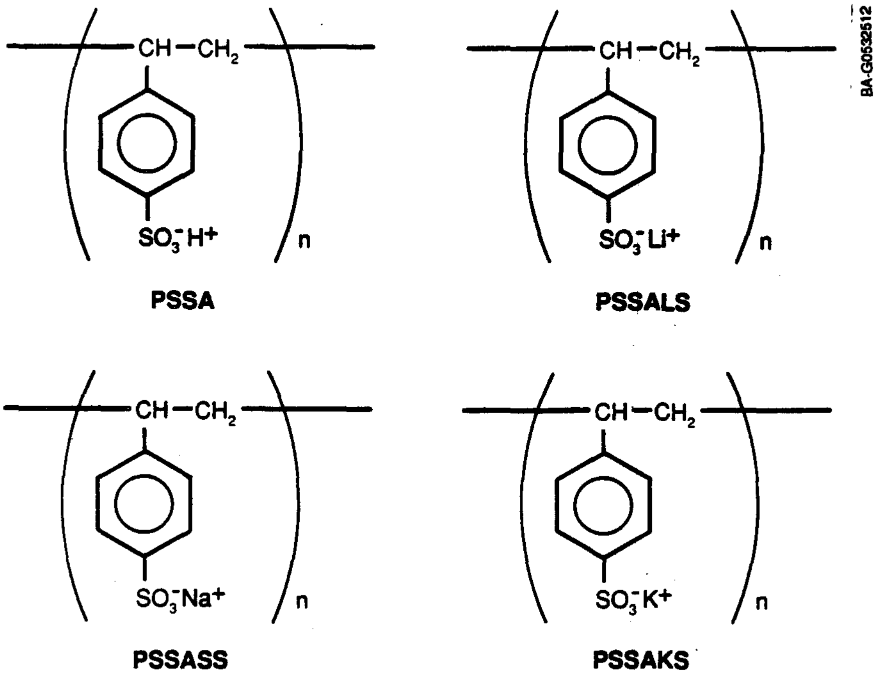
Procedures were developed prior to writing this report for using the QCM apparatus for studying the adsorption and desorption kinetics as well as the cyclic stability of the sorption performance. These procedures are described in Appendix F.

2.5 Procedure for Mounting Polymers on QCs for Sorption Performance Measurements

Standard procedures were developed in 1986 and 1987 for mounting polymers on QCs for study in the QCM apparatus. The polymers are adherently coated onto the crystals using solvent evaporation procedures. The polymer is dissolved in water or a water-ethanol mixture and then added dropwise to the gold film on a QC. The mass of polymer is controlled by the number of drops and its uniformity by how the solution spreads over the gold surface. The procedures were described in Czanderna (1988, Section 4.2).

3.0 PREPARATION OF POLYMERS

Polymers studied for sorption performance were obtained from commercial sources, preparation procedures developed internally for modification studies, and synthesis procedures for preparing one new desiccant polymer. The sources of the polymers and the preparation procedures are discussed in this section. We focused our modification activities this year on PSSA and the alkali ionic salts of PSSA, as shown in Figure 3-1.



PSSA PSSALS

PSSASS PSSAKS

Figure 3-1. Structural repeating units for PSSA, PSSALS, PSSASS, and PSSAKS, where n is the number of repeating units

Three variables in these structures can influence the isotherm shape and capacity, i.e., the MW, percent sulfonation, and counterion (cation) present. The MW depends on the number of repeating units n, the percent sulfonation, and the counterion present. The percent sulfonation specifies the number of SO_3^- groups attached to the phenyl group (as shown), where 100% corresponds (ideally) to one SO_3^- per phenyl group. A polymer that is "20% sulfonated" simply means that only one of every five phenyl groups has an SO_3^- group attached. The percent sulfonation can exceed 100% because of multiple sulfonation of the phenyl groups, e.g., at the ortho or meta positions of the structures shown in Figure 3-1. The alkali ionic salts of PSSA are made by exchanging the H^+ of PSSA with a different counterion, as shown in Figure 3-1 for Li^+, Na^+, and K^+. During 1989, we studied PSSA, polystyrene sulfonic acid lithium salt (PSSALS), PSSASS, polystyrene sulfonic acid potassium salt (PSSAKS), polystyrene sulfonic acid ammonium salt (PSSAAS) (ammonium salt, NH_4^+), and SPSS. SPSS is a commercially available form of PSSASS with a narrow MW distribution at various MWs and is 90% sulfonated. During 1988, we showed that more favorable isotherm shapes and capacities are obtained for MWs between 5000 and 66,100 and for sulfonation percentages of 50% to 80%, although further work to optimize the latter is clearly needed.

3.1 Commercially Available Polymers

Commercially available polymers were used to study the influence of the counterion on the isotherm shape and capacity because they are readily available. The sources of commercially available polymers used for sorption studies are given in Table 3-1. The PSSAAS and CSSS polymers were studied as part of our interactions with the Cargocaire Engineering Corporation. The principal problem with the commercially available PSSA and PSSA salts is that the sulfonation percentage is not available from the manufacturer, nor is it known how carefully the sulfonation is controlled among various lots of the material. However, the loss of a key polymer scientist (H. Neidlinger) to the project in March required an alternative approach to ensure progress in our studies of PSSA salts. Furthermore, control of the synthesis methods is obviously lost, and it is clearly important that these procedures be regimented to obtain confident correlations between the water sorption properties and the materials properties (MW, percent sulfonation, and counterion). Arrangements were made during the year with a subcontractor to prepare modifications of PSSA and synthesize one new polymeric material for the task. The statement of work is attached as Appendix G. Because the 5-month effort was initiated by the subcontractor, Eastman Kodak, on October 17, 1989, the sorption characterization results of its preparations will be reported in the next annual report.

3.2 Preparation of Partially Sulfonated Polystyrenes

Most of the polymers studied this year are listed in Section 3.1. However, some of the polymers studied were prepared at SERI in 1988. The information provided in this section is the same as in a previous report (Czanderna and Neidlinger 1990) but is given here for convenience.

3.2.1 Materials

The partial sulfonation reaction of PS requires careful attention to several details, specified in Section 4.1, to avoid secondary reactions, such as cross-linking. Basically, finely divided PS* powder is dissolved at room temperature into dichloroethane (1% to 2%), to which the proper amount of chlorosulphonic acid (0.2-0.8 mol-equivalent) is added under vigorous stirring. As sulfonation proceeds, the PS becomes insoluble, and the reaction is complete in 15 to 30 min. Separation of the polyelectrolyte is then accomplished by water extraction, neutralization, dialysis, and solvent evaporation.

Characteristic details of the syntheses are given below for sample MK1-88-3/4: 1.279 g PS (MW = 6000) was dissolved in 102-ml dichloroethane in a 1-l three-neck, round-bottom reaction flask. Then, 0.6 mol-equivalent (0.84 g) chlorosulphonic acid in 100-ml dichloroethane was added dropwise with vigorous stirring at room temperature over a 3-h period. The reaction was allowed to proceed for another 30 min, yielding a straw-colored solution and a precipitate on the side of the reaction flask. While stirring, we added 100 ml of deionized water to extract the water-soluble reaction product.

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*The polystyrene samples used were from Polysciences: MW 6000 (lot #62716) and MW 50,000 (lot #54689).

Table 3-1. Commercially Available Polymers Characterized for Water Vapor Sorption Performance

Acronym	Source	Polymer	Comments
CSSS	Scientific Polymer Prod., Inc. Cat. #023	Cellulose sulfate sodium salt	Isotherms have neglible hysteresis
PSSA	National Starch Co. VERSA-TL 72	Polystyrene sulfonic acid	MW = 70,000, pH = 1.0
PSSALS	National Starch Co. VERSA-TL 73	Polystyrene sulfonic acid lithium salt	MW = 70,000, pH = 4.0
PSSAKS	National Starch Co. VERSA-TL 126	Polystyrene sulfonic acid potassium salt	MW = 120,000, pH = 4.0
PSSAAS	National Starch Co. VERSA TL 125	Polystyrene sulfonic acid ammonium salt	MW = 12,000, pH = 4.0
PSSASS	National Starch Co.	Polystyrene sulfonic acid sodium salt	
	VERSA-TL 3		MW = 20,000, pH = 7.0
	VERSA-TL 7		MW = 15,000, pH = 7.0
	VERSA-TL 77		MW = 70,000, pH = 4.0
	NARLEX D-72		MW = 12,000, pH = 6.0
	NARLEX D-82		MW = 25,000, pH = 6.0
SPSS	Scientific Polymer Prod., Inc. Cat. #623	Sodium polystyrene sulfonate	MW = 66,100

An excess of sodium carbonate (0.63g Na_2CO_3 in 100 ml H_2O) was added to neutralize the free acid. After standing overnight, the organic (MK1-88-4) and aqueous (MK1-88-3) layers were separated and filtered, and the solvents were removed with a Rotovap.

A complete listing of all preparations of PSSASS is given in Table 3-2. Those in Series 1 were prepared by neutralizing the acid form of PSSA with an excess of sodium carbonate followed by dialysis purification against pure water. Those in Series 2 were prepared by neutralizing the acid form of PSSA with an equivalent concentration of sodium hydroxide.

3.2.2 Purification

The water-soluble sodium salts of the partially sulphonated PS from Series 1 were purified from excess sodium carbonate via extensive dialysis against deionized water using Spectra/Por 6 membranes (MW-cutoff 1000). The dialysis procedure took about 4 to 5 days and was monitored by conductance measurements. The dialyzed material was isolated on a Rotovap and dried to constant weight in a vacuum oven at 70°C. The water-insoluble products (from the organic layer) were washed repeatedly with deionized water and vacuum dried to constant weight, as mentioned previously.

The water extracts from the acidic reaction products of Series 2 were carefully neutralized with 1 N NaOH by potentiometric titration to pH 7 and used in the sorption experiments without further purification.

3.2.3 Characterization

The degree of sulfonation (or mol-fraction of sulfonate groups) was determined from elemental analysis performed by Huffmann Laboratories, Golden, Colorado. A typical analysis for a PSSASS (MK2-88-27) is 50.7% C, 4.8% H, 11.6% O, and 9.7% S. The theoretical analysis for a 100% sulfonated PSSASS (one sulfonate per phenyl group) is 3.4% H, 46.4% C, 15.5% S, 23.2% O, and 11.1% Na.

Ultraviolet absorption spectra and extinction coefficients in aqueous solution were measured with a Perkin-Elmer Lambda 9 spectrometer. By taking the equivalent weight of the polyelectrolyte as $M = 103\alpha + 104$, corresponding to $(C_8H_7SO_3Na)_\alpha\ (C_8H_7)_{1-\alpha}$, the equivalent extinction coefficients at the maximum 261 nm were calculated.

Table 3-2. All Preparations of PSSASS

Sample	Molecular Weight of Parent PS	Mol-% Sulfonation		Solubility
		Feed	Product[a]	
Series 1[b]				
MK1-88-1	6,000	40	56	H_2O
MK1-88-2	6,000	40	--	DCE
MK1-88-3	6,000	60	83	H_2O
MK1-88-4	6,000	60	--	DCE
MK1-88-5	6,000	80	67	H_2O
MK1-88-6	6,000	80	--	DCE
MK1-88-7[3]	6,000	80	--	H_2O
MK1-88-8[3]	6,000	80	--	DCE
MK1-88-9	6,000	20	--	H_2O
MK1-88-10	6,000	20	44*	EtOH/H_2O
MK1-88-11	50,000	40	36	H_2O
MK1-88-12	50,000	40	--	DCE
MK1-88-13	50,000	60	75*	H_2O
MK1-88-14	50,000	60	--	DCE
MK1-88-15	50,000	80	51	H_2O*
MK1-88-16	50,000	80	--	DCE
MK1-88-17	50,000	20	20	EtOH/H_2O
MK1-88-26	6,000	20	--	EtOH/H_2O
Series 2[c]				
MK2-88-27	6,000	60	58	H_2O
MK2-88-28	6,000	60	--	DCE
MK2-88-29	6,000	80	84	H_2O
MK2-88-30	6,000	80	--	DCE
MK2-88-31	6,000	40	48	H_2O
MK2-88-33	6,000	40	--	DCE
Series 3[d]				
RG19-52-2	6,000	40		H_2O
RG19-52-3	6,000	80		H_2O
RG19-52-4	6,000	60		H_2O

[a] Determined by elemental analysis; marked (*) samples were not completely homogeneous.

[b] Prepared by neutralizing the acid form with an excess of Na_2CO_3 and purified by dialysis against pure water.

[c] Identifies acid form (not neutralized).

[d] Prepared by neutralizing the acid form in Series 2 with an equivalent concentration of NaOH.

4.0 EXPERIMENTAL RESULTS AND DISCUSSION OF SORPTION MEASUREMENTS ON DIFFERENT POLYMERS

4.1 Isotherms of Polymers Studied

Of the criteria for a candidate ADM, the determination of an adsorption isotherm provides four important pieces of data: (1) the shape, (2) the capacity and possible capacity change between 5% and 60% R.H., (3) the absence or presence of hysteresis between the adsorption and desorption legs of the isotherm, and (4) the kinetics of the sorption or desorption process after each pressure change. Points 1, 2, and 3 are discussed in the following subsections on the data that were obtained. Data for (4) are discussed in Section 4.6. In almost all cases, there was no hysteresis, so the data in the figures represent both adsorption and desorption without making a distinction for the various data points. One exception is noted and discussed.

4.2 Isotherms of SERI-Prepared PSSA

Degradation in Water Vapor Sorption Capacity of PSSA. In our 1988 progress report, we presented isotherms for 60% and 80% sulfonated PSSA prepared at SERI (MK2-88-29 and -31, Table 3-2) that had capacities of 120% and 400% at 50% R.H., respectively (Czanderna and Neidlinger, 1990). We cautioned that these results had to be repeated; this year, we obtained some interesting results. For the first two months of 1989, our QCM apparatus could not be used because of a defective turbomolecular pump (after 26,000 h of operation) and several defective parts supplied by Balzers on replacement part purchases. Three months elapsed from the time the measurements were reported last year (Figure 4-6, Czanderna and Neidlinger 1990) to the point where we could repeat the isotherm determinations. The PSSA isotherms are presented in Figure 4-1, which includes a plot of MK2-88-29 from 12/88, four new determinations of this PSSA in March and April of 1989, and one for VERSA TL 72 (Table 3-1). There was an enormous loss in capacity and a change in the isotherm shape between 12/88 and 3/16/89. Note that the plot for 12/88 is multiplied by 0.1, so the capacity loss ranged from 10 to 15 times greater during this 3-month period. The additional measurements of samples from the same PSSA preparation show the isotherm shape changes; the capacity loss was 100 to 200 times greater when measured on 4/28/89. Clearly, some degradative mechanism is causing the capacity loss, but it is not known. Methane sulphonic acid (MSA) is known to oxidize to a sulphate in condensed media (Clegg and Brimblecombe 1985) but we do not know the sorption properties of sulphates of PSSA, if PSSA oxidizes as does MSA, or if the degradation mechanisms are similar. The PSSA was in a closed container with room air filling about half the bottle. The plot for VERSA TL 72 is similar to those obtained after 4 months of "aging" SERI-prepared MK2-88-29. Although we are interested in learning why the PSSA degrades, the available time on the task has precluded our seeking an understanding of the degradation phenomenon. As a practical matter, any desiccant used in CDCSs must be stable for months in air, and the PSSA we have studied is not. We made several attempts in 1987 to measure PSSA isotherms, but we lost interest when their capacities were found to be less than 5%. This surprised us at the time, but we now at least have some empirical evidence that the sorption capacity of PSSA is time dependent. As is well known for the QCM (Lu and Czanderna 1984), there is no time-dependent drift in the calibration constant or the oscillator supply that causes changes in this or other results we present.

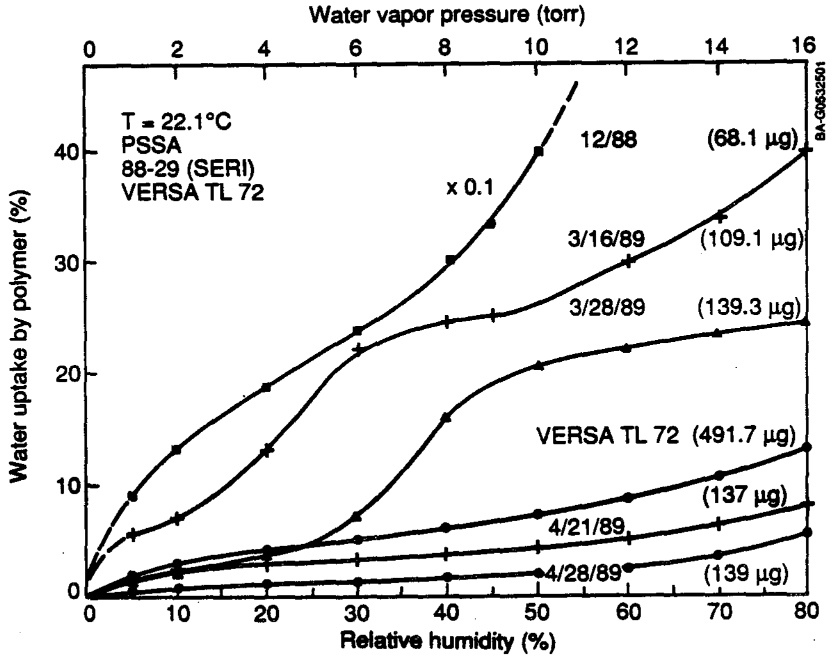

Figure 4-1. Water vapor isotherms at 22.1°C for PSSA, SERI MK2-88-29 and National Starch VERSA TL 72

Sorption on PSSA Retained in the Organic Solvent. As a matter of interest, isotherms of PSSA retained in the dichloroethane solution were determined. In our previous report (Czanderna and Neidlinger 1990), we showed that PSSASS retained in dichloroethane had low capacity and poor isotherm shapes. The isotherms for PSSA (Figure 4-2) show similar behavior. The isotherm shapes are Type 2 with a low c value (88-7) or Type 3 (88-28), which are both undesirable for DCSs. A summary of how Type 2 isotherms can become Type 3 isotherms, depending on the c value in the two-parameter BET equation, was given in Adamson (1990). Although the capacity changes from 5% to 60% R.H. are adequate or quite good, the isotherm shape is not desirable. With these results, combined with those in our previous report (Czanderna and Neidlinger 1990), it is probably safe to conclude that ionic polymers that are soluble in organic solvents such as dichloroethane will not possess desirable isotherm shapes.

4.3 Isotherms of Alkali Ionic Salts of PSSA

Isotherms obtained for PSSALS, PSSASS, PSSAAS, and PSSAKS are shown in Figures 4-3 through 4-5. The reproducibility of the PSSALS isotherms (Figure 4-3) is excellent for three different sample sizes. For the 244 µg sample that has the lowest capacity, the data were taken in a separate earlier run. Although there may be a number of reasons for the observed difference, any explanation would be speculative. Therefore, we focus our interpretation on the three samples that yielded reproducible results. The isotherms are all "high c" Type 2, and the capacity change of more than 30% between 5% and 60% R.H. is higher than for any of the other VERSA TL or NARLEX samples. Although the isotherms are not Type 1 moderate, their shape is relatively desirable from 5% to 50% R.H. and are only inflected upward above 50% R.H.

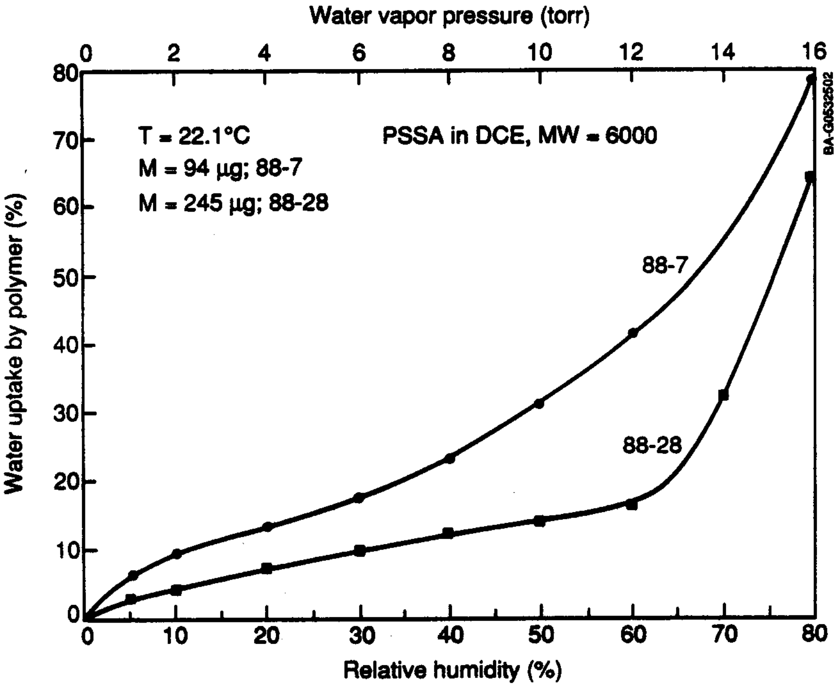

Figure 4-2. Water vapor isotherms at 22.1°C for SERI MK1-88-7 and MK2-88-28 PSSA retained in a dichloroethane solution

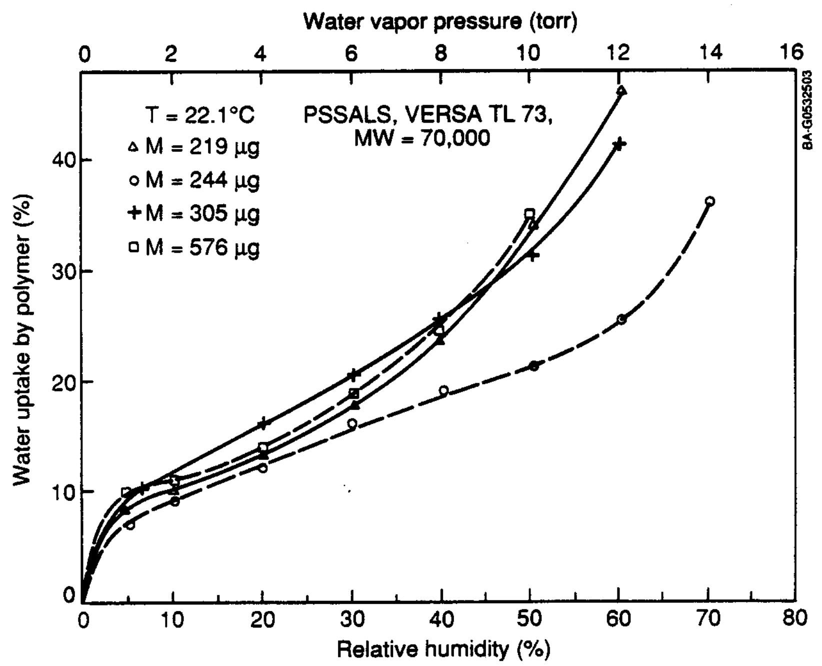

Figure 4-3. Water vapor isotherms at 22.1°C for four different sample sizes of PSSALS, National Starch VERSA TL 73, MW = 70,000

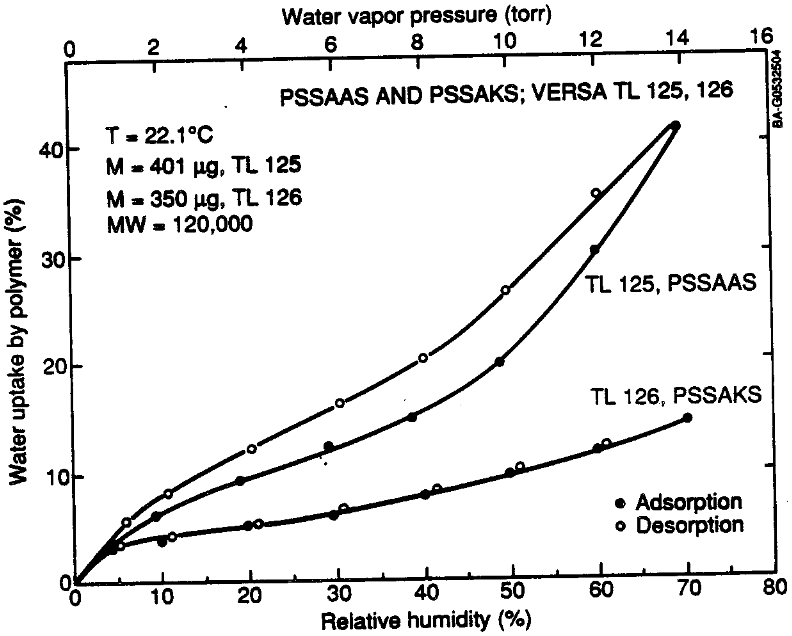

Figure 4-4. **Water vapor isotherms at 22.1°C for PSSAAS and PSSAKS, National Starch VERSA TL 125 and 126, respectively, MW = 120,000**

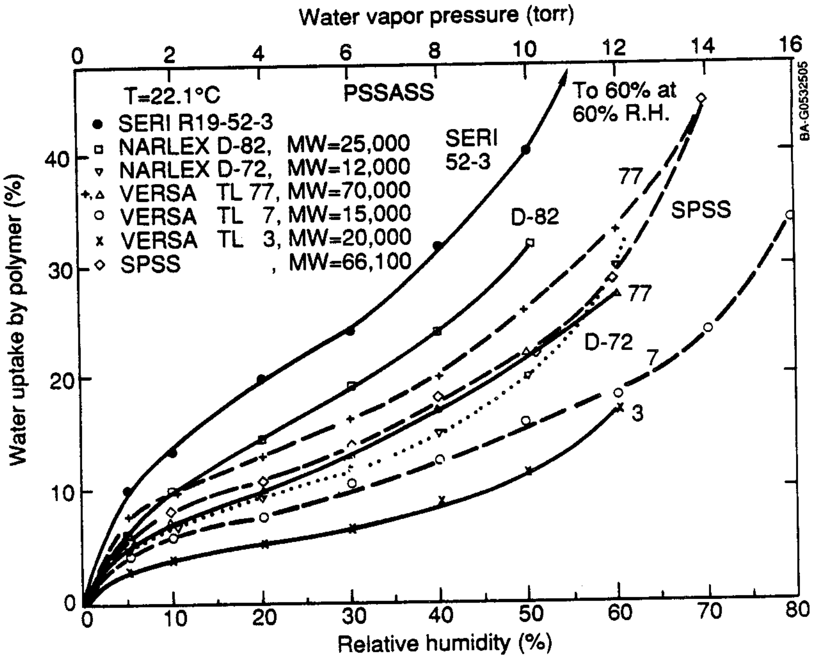

Figure 4-5. Water vapor isotherms at 22.1°C for PSSASS; SERI R19-52-3; National Starch NARLEX D-82 and D-72; and VERSA TL 3, 7, and 77. **A prior result with Scientific Polymer SPSS, 90% sulfonated, is added for comparison (Czanderna 1988).**

The isotherms for PSSAAS and PSSAKS are both Type 2 but have other undesirable characteristics. As expected, the capacity change from 5% to 60% R.H. is rather low (ca. 10%) for PSSAKS. The isotherm for PSSAAS exhibits hysteresis. Furthermore, the isotherm shape indicates weaker water vapor-ion interactions than other alkali ions. Thus, neither the K^+ as an alkali ion nor NH_4^+ as a monovalent counterion provide ionic salts of PSSA that are as good as PSSASS or PSSALS.

Isotherms for six commercially available forms of PSSASS are shown in Figure 4-5, where SERI R19-52-3 is also plotted (Czanderna and Neidlinger 1990). All the isotherms are Type 2 in shape, but the different preparations have different capacities for the same generic material. For example, the Narlex D-82 has a capacity change from 5% to 50% R.H. of 26%, but the VERSA TL 7 only has a change of 12%. These results are not unexpected because the water vapor sorption capacity depends strongly on the percent sulfonation and the counterion present. Because the same counterion is used in all the samples, the variations observed probably result from the percent sulfonation (a major cause), molecular weight (a minor cause), possible impurities, and unknown reasons. These are the same reasons that prompted us to undertake our own synthesis and modification efforts in early 1988; however, these efforts could not be continued for most of 1989 without a resident polymer synthesis and modification expert.

For optimum research results, the variables that affect the performance properties of the desiccant materials must be optimized and kept under control. The latter will be done with samples obtained from Kodak, but we cannot be certain the optimum product has been specified because of the minimal data we have available to us. We hope the new samples will be as good or better than SERI sample R19-52-3, which clearly provided us with the best isotherm of the various PSSASS samples we have measured to date.

Finally, representative isotherms of PSSA, PSSALS, PSSASS, PSSAKS, and CSSS are compared in Figure 4-6. The range of capacities for PSSASS is represented by the plots for VERSA TL 7 and 77. CSSS has exhibited excellent cyclic reproducibility and rapid water vapor sorption kinetics and has a slightly better than marginal capacity change from 5% to 60% R.H. All isotherms have the relatively desirable Type 2 shape, with the capacity change for the PSSALS slightly better than PSSASS; both PSSALS and PSSASS (optimized) are considerably better in their capacity change than PSSAKS. Of course, PSSA provides both a better shape and significantly better capacity change, but has problems with degradation, as discussed in Section 4.2.

Our hypothesis on the influence of the counterion is supported by the data that show the capacity follows the order of $H^+ > Li^+ \gtrsim Na > K^+$; i.e., the largest water uptake capacity is obtained for PSSA with the smallest ion (H^+). The sorption is thought to occur in the ionic polymer primarily by ion-dipole interactions that result in the formation of a cluster of water molecules around the relatively isolated counterion. Smaller ions will produce stronger interactions and permit larger clusters of water to form, thus increasing the sorption capacity of the polymeric ionic salt. We have not attempted to estimate an optimum sulfonation percentage, but there surely will be an optimum, where cluster formation will be sterically limited by too many counterions. A calculation of the optimum sulfonation percentage and the

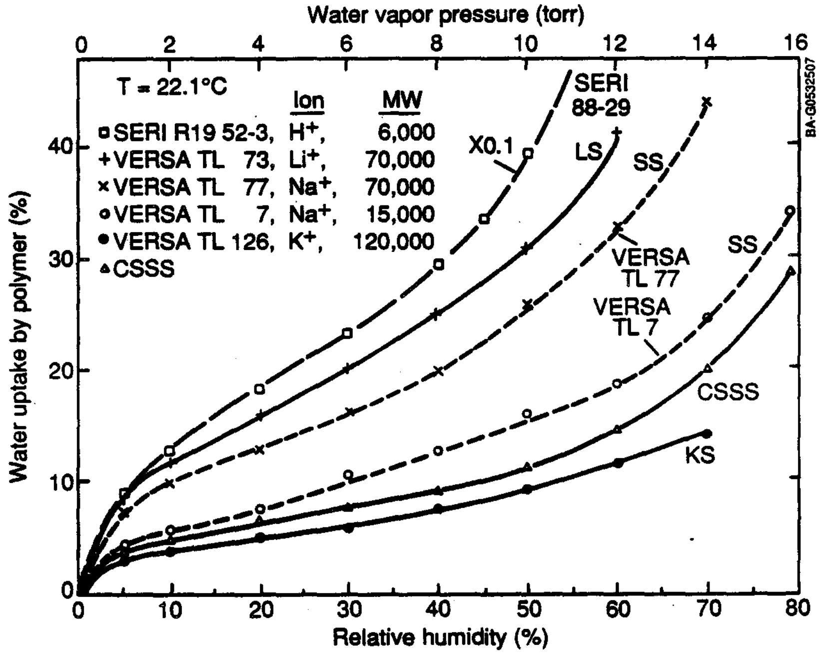

Figure 4-6. Water vapor isotherms at 22.1°C for PSSA (SERI R19-52-3), PSSALS (VERSA TL 73), PSSASS (VERSA TL 7 and 77), and PSSAKS (VERSA TL 126). An isotherm for CSSS (Scientific Polymer) from prior work is also plotted (Czanderna 1988).

attachment positions of the counterions on PSSA before forming the salt could be of great interest to this research. A physical organic chemistry theorist might be a good choice for performing such a calculation.

4.4 Isotherms of PSSA Alkali Salts at 17°, 22.1° and 27°C

Isotherms were obtained at 17°, 22.1°, and 27°C for PSSALS, PSSASS, SPSS, and PSSA. These were obtained to determine if there are significant temperature effects on the isotherm shape and on the capacity change between 5% and 60% R.H. Another purpose was to determine if the temperature range chosen is appropriate for determining the heats of adsorption. The isotherms at 17°, 22.1°, and 27°C are shown for PSSALS in Figure 4-7, PSSASS in Figure 4-8, and SPSS in Figure 4-9. As is discussed later, the PSSA isotherms are of little interest and so are not plotted.

The isotherm shape clearly depends on temperature, especially, for PSSASS and the 90% sulfonated form, SPSS. At 27°C, the isotherms are already transformed to a "low c" BET Type 2 isotherm, or possibly, a Type 3. In the case of PSSALS, the shape remains as Type 2 but with a reduced capacity. These results are similar to those obtained for acrylamide-carboxyl modified by H. Bizot, A. Cairault, and N. Mouhous-Riou (1987), who showed a transformation occurs from BET Type 2 to Type 3 between 20° and 78°C. These results are especially significant for DCS applications. From the parametric studies (Collier, Cale, and Lavan 1986), it was concluded that a Type 1 moderate (or Type 1 extreme) is the best shape for the adsorption step, and a Type 3 extreme is the best shape during regeneration or desorption of water. The results for PSSASS show that this material provides an acceptable shape for

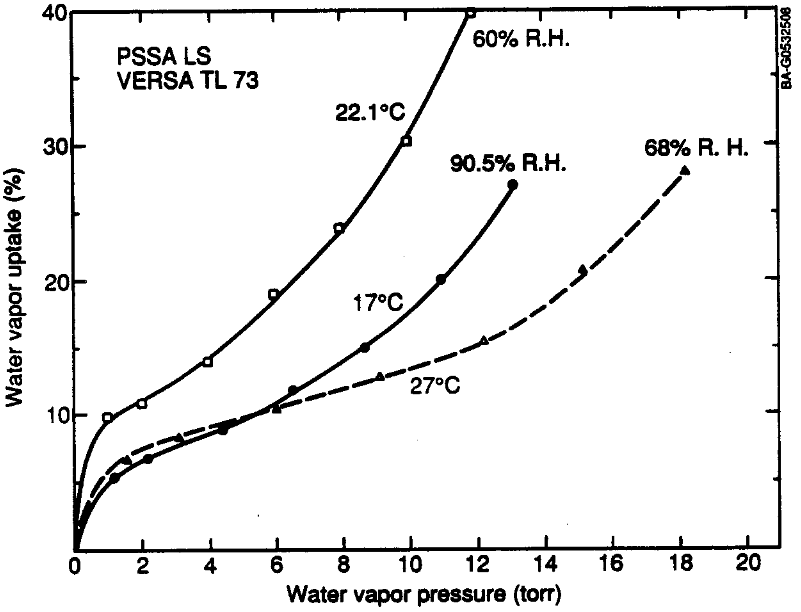

Figure 4-7. Water vapor isotherms at 17°, 22.1°, and 27°C for PSSALS, National Starch VERSA TL 73

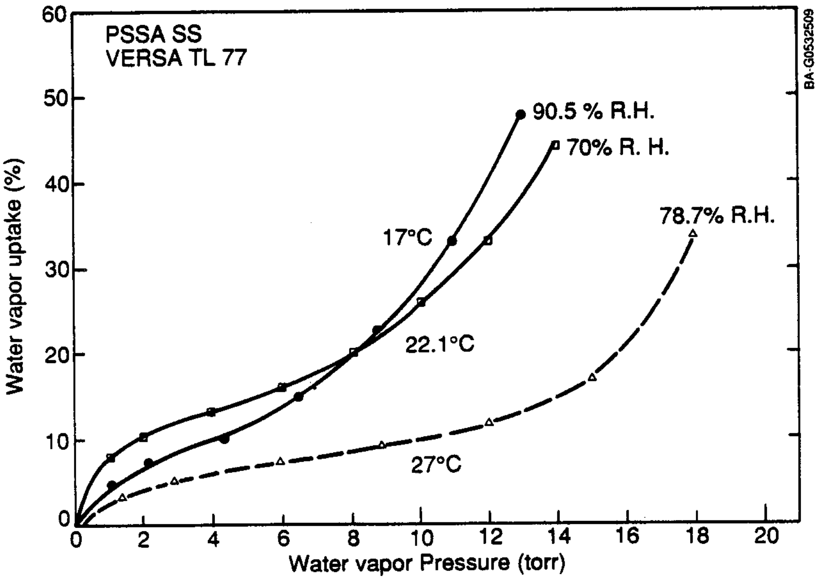

Figure 4-8. Water vapor isotherms at 17°, 22.1°, and 27°C for PSSASS, National Starch VERSA TL 77

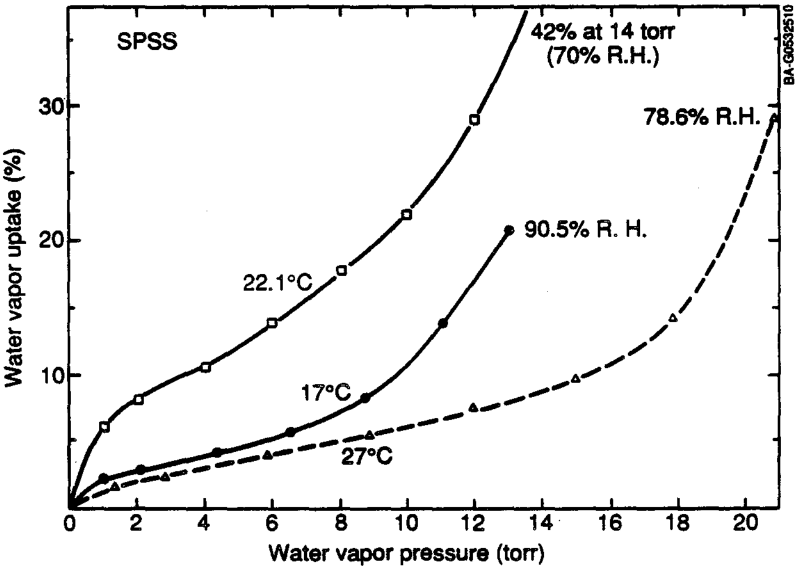

Figure 4-9. Water vapor isotherms at 17°, 22.1°, and 27°C for 90% sulfonated SPSS, Scienctific Polymer, MW = 66,100

adsorption and a more desirable shape for regeneration, with only a 5°C temperature increase. When isotherms can be determined at 50° to 80°C, the trend suggests that this polymeric material may have an ideal shape for regeneration. I am not aware of any similar temperature influences for inorganic desiccants, although the same time of effect should be anticipated but over a wider temperature range. This is because the controlling interactions are different between inorganic materials (dipole-surface interaction) and cationic polymers (dipole-ion interaction). More work is clearly needed to understand the influences of dipole-"material" interactions for desiccants, but the temperature dependence observed for PSSASS (and the trend for PSSALS) is very favorable for solar-regenerated DCS.

In regard to the capacity change, there are clearly differences in the capacity for the isotherms in Figures 4-7 through 4-9. Differences were expected but not of the form obtained. We plotted in Figure 4-10 the capacity at 60% R.H. for PSSALS, PSSASS, SPSS and from the raw data for PSSA. The uptake for the three temperatures is largest at 22.1°C, so a real maximum must lie somewhere between 17° and 27°C. A result similar to Figure 4-10 will also be obtained if the data are plotted at constant water vapor pressure, e.g., 2, 4, 6, or 8 torr for all three samples and 10 and 12 torr for PSSALS and SPSS. We had expected a monotonic decrease in the capacity at a constant R.H., which could then be used to determine the isosteric heat of adsorption. Future work could be directed at determining the temperature that yields an isotherm of maximum capacity to support defining optimum CDCS operating temperatures.

In regard to the temperature range, determining the isosteric heat of adsorption requires that the pressure at a constant capacity must increase with increasing temperature. This is clearly not the case, as suggested by Figure 4-10, but can be explicitly deduced visually by scanning the three

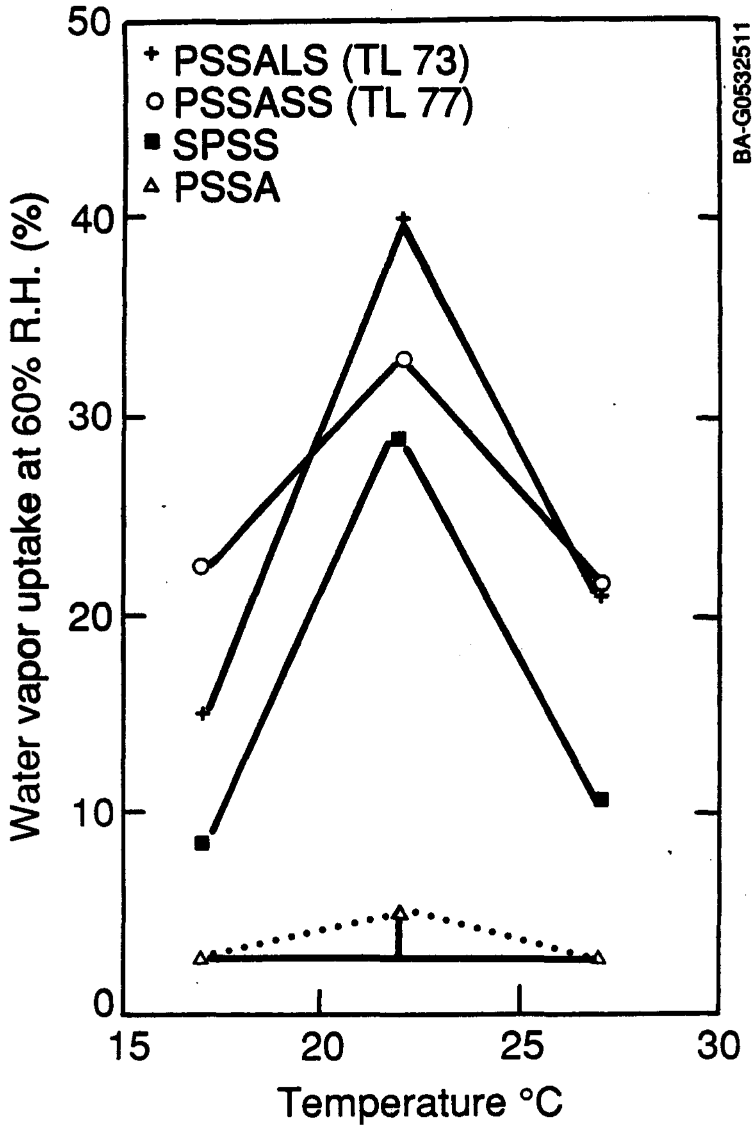

Figure 4-10. Percent water vapor uptake at 60% R.H. for PSSALS, PSSASS, and SPSS at 17°, 22.1°, and 27°C, taken from Figures 4-7, 4-8, and 4-9. The lines are to guide the eye only.

isotherms for each sample at constant capacity, e.g., PSSALS at 15% water vapor uptake where the isotherms encountered (with increasing pressure) are 22.1°, 17°, and 27°C rather than 17°, 22.1°, and 27°C. We do not have an explanation for the observed behavior but can conclude that heats of adsorption must be deduced from sets of isotherms that show monotonic increases in pressure at constant capacity and increasing isothermal temperatures. As shown, the data would produce negative heats of adsorption below 22.1°C, which, of course, doesn't make sense. If the isotherms at 22.1°C are really the maximum capacity curves, then heats of adsorption might be obtained from adsorption at 22.1°, 27°, and 35°C, for example. Clearly, more work needs to be done to explain these unexpected results.

4.5 Isotherms of CSSS

Two isotherms were determined for CSSS obtained from the Aldrich Chemical Co. They are compared in Figure 4-11 with a representative isotherm of CSSS from Scientific Polymers Inc. that was obtained in 1987. The latter was found to be extremely reproducible, free of hysteresis, and cyclically stable for as many as nine cycles. As is seen, the recent results are similar for both sources of CSSS, but the Type 2 isotherms for the Aldrich Chemical CSSS have about 3% more capacity of uptake at 60% R.H. The kinetic studies on CSSS reported in Section 4.6 were taken on another sample of the Aldrich Chemical CSSS. The capacity change for this CSSS between 5% and 60% R.H. is about 10%, or 2% to 4% more than the minimum needed as suggested by Collier, Cale, and Lavan (1986).

4.6 Kinetics of Adsorption and Desorption

The purposes of this subsection are to illustrate some of the capabilities of the new DAQS and to show that the rates of adsorption and desorption for several polymers are sufficiently rapid for use in CDCSs. The most common uses of the DAQS are to obtain isotherms, measure adsorption and desorption kinetics, and measure mass losses during the initial evacuation of the samples.

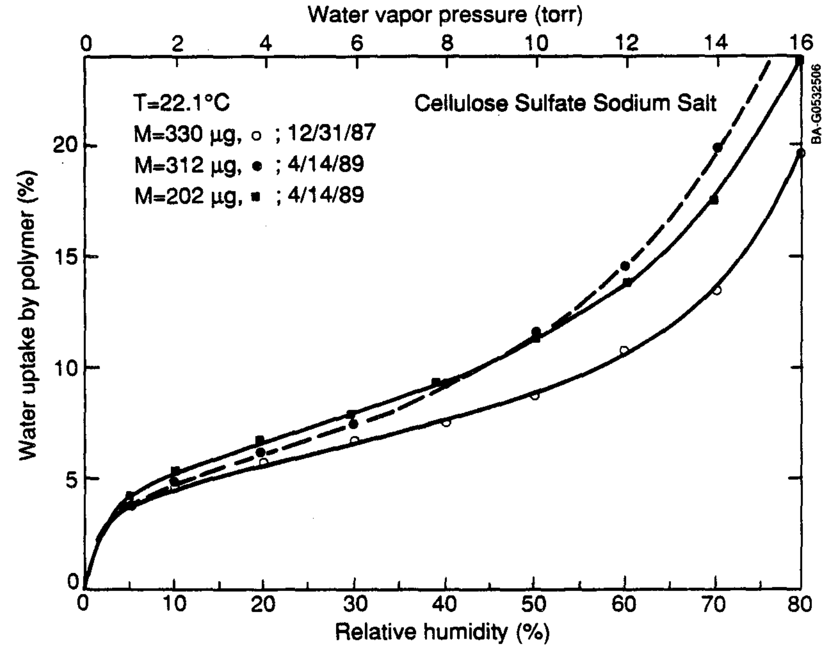

Figure 4-11. Water vapor isotherms at 22.1°C for two samples of CSSS, Aldrich Chemical Co. An isotherm from prior work with CSSS from Scientific Polymer is plotted for comparison (Czanderna 1988).

The data shown in Figure 4-12 are for four different-sized samples of CSSS and are displayed in real time. The incremental increases or decreases in water vapor pressure during adsorption and desorption were made at ca. 2000- to 3000-s intervals. After each pressure increase, there is a rapid mass gain followed by a plateau indicating no further mass gain. The reverse process is observed during desorption. (The vertical lines at about 11,000 s (adsorption) and 13,500 s on desorption are for a sample that failed during adsorption and reactivated during desorption). All the data can be retrieved (and printed), so the equilibrium mass changes between two pressure points can be calculated from the actual data rather than the plot. For each pressure increment or decrement, the data can be retrieved and displayed between any two masses and any two times. Thus, the rate of approach to equilibrium at any pressure can be displayed (and printed if desired) to determine when equilibrium has been reached. For screening potential new polymeric desiccants, these kinetic measurements are used to eliminate a potential candidate if the criteria for use in a CDCS are not met (e.g., 90% of the capacity change in 5 min or less). Most isotherms are determined from nine incremental pressure increases at about 45-min intervals followed by nine pressure decreases the following day. The overnight stability can be noted from the final plateaus for adsorption and the initial plateaus for desorption (e.g., 8,000 ng/cm^2 for the sample with the least uptake).

A more crucial test for a candidate polymer is the kinetics of adsorption and desorption for pressure increases from 5% to 60% R.H. followed by a sudden pressure decrease to 5% R.H. The absolute pressures for these changes at 22.1°C are 1 to 12 to 1 torr. The data in Figure 4-13 show the mass gain and mass losses for PSSASS, PSSAKS, and PSSAAS. As is seen, the adsorption was completed in 180 s and the desorption in about 120 s for a total of 300 s. When the time for only 90% of the mass change on adsorption and desorption is used, the total time is decreased from about 300 s to about 180 s. Both these times are less than the 600 s per revolution typically used for desiccant wheels in CDCSs (see Appendix B).

Concerning relative adsorption and desorption times, the absolute values measured on a material only a few microns thick will yield the fastest possible times for the material itself, as pointed out in the next to last paragraph of Appendix C. Incorporating a polymer into an engineering design, such as a desiccant wheel (last paragraph, Appendix C), surely will result in slower rates than those obtained with samples mounted on our QCM. We do not know how much slower the rate will be when a polymer is used in a desiccant wheel than for the pure material. However, we can measure the adsorption and desorption times and rank the desiccants based on their total time because there must be some empirical factor connecting the sorption performance of the pure material with the same material used in a desiccant wheel, or any other engineering configuration. The time comparisons made must be considered from the perspectives outlined above and in Appendix C.

The data shown in Figure 4-14 are similar to those shown in Figure 4-13 but are for three different sample sizes of CSSS. The rates of adsorption and desorption are even faster for CSSS than for any of the three polymers shown in Figure 4-13. To examine the kinetics for CSSS in more detail, we carried out additional measurements for increases from 1 to 12 torr and decreases from 12 to 1 torr at 17°, 22.1°, and 27°C. These data are shown in Figures 4-15, 4-16, and 4-17, respectively. We estimated the times required for both 90%

and the entire total mass change for the sample marked A or D in the three figures and listed them in Table 4-1. We have not done this for all four samples because by visual inspection, all four would yield similar results. As stated before, the sum of the times for both adsorption and desorption is much less than 360 s at all three temperatures.

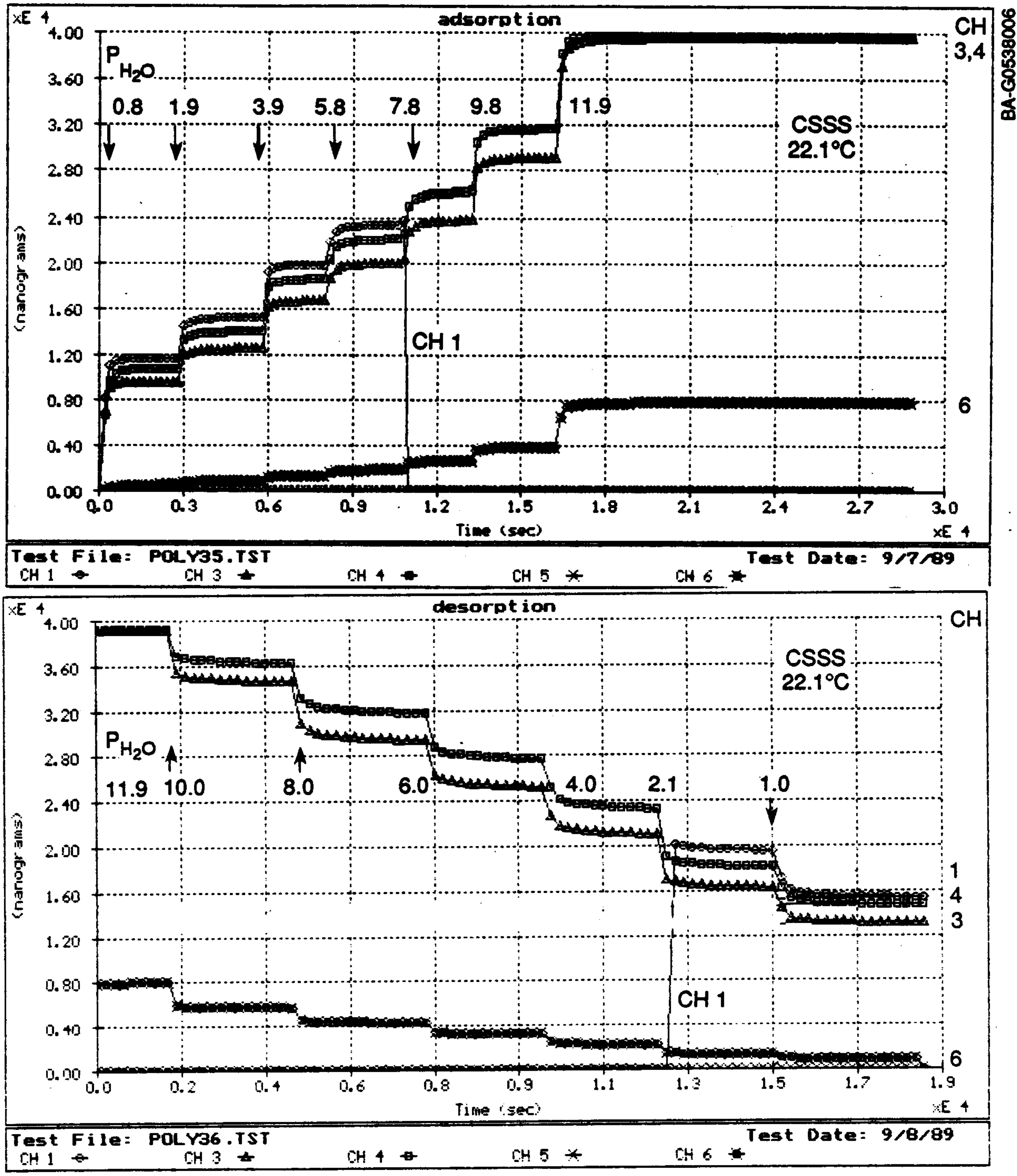

Figure 4-12. The mass change versus time at 21.1°C of CSSS during absorption and desorption of water vapor, as obtained with the DAQS.

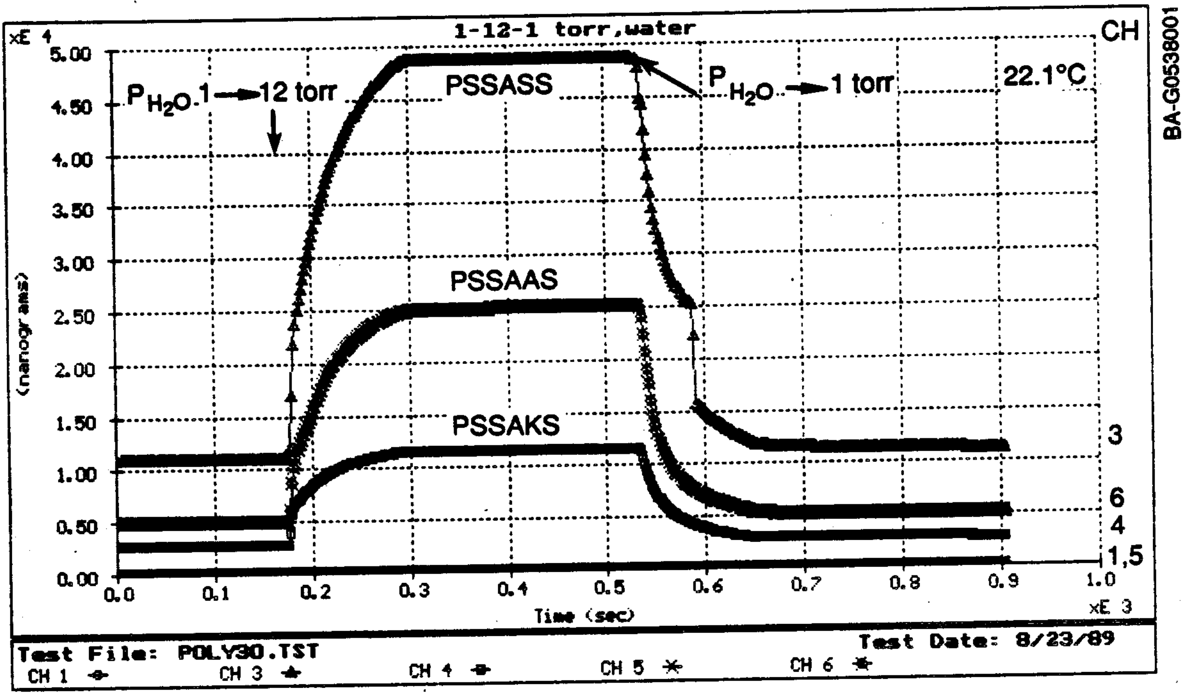

Figure 4-13. The mass change versus time at 22.1°C of PSSASS, PSSAAS, and PSSAKS after an increase in water vapor pressure from 1 to 12 torr and a decrease back to 1 torr, as obtained with the DAQS.

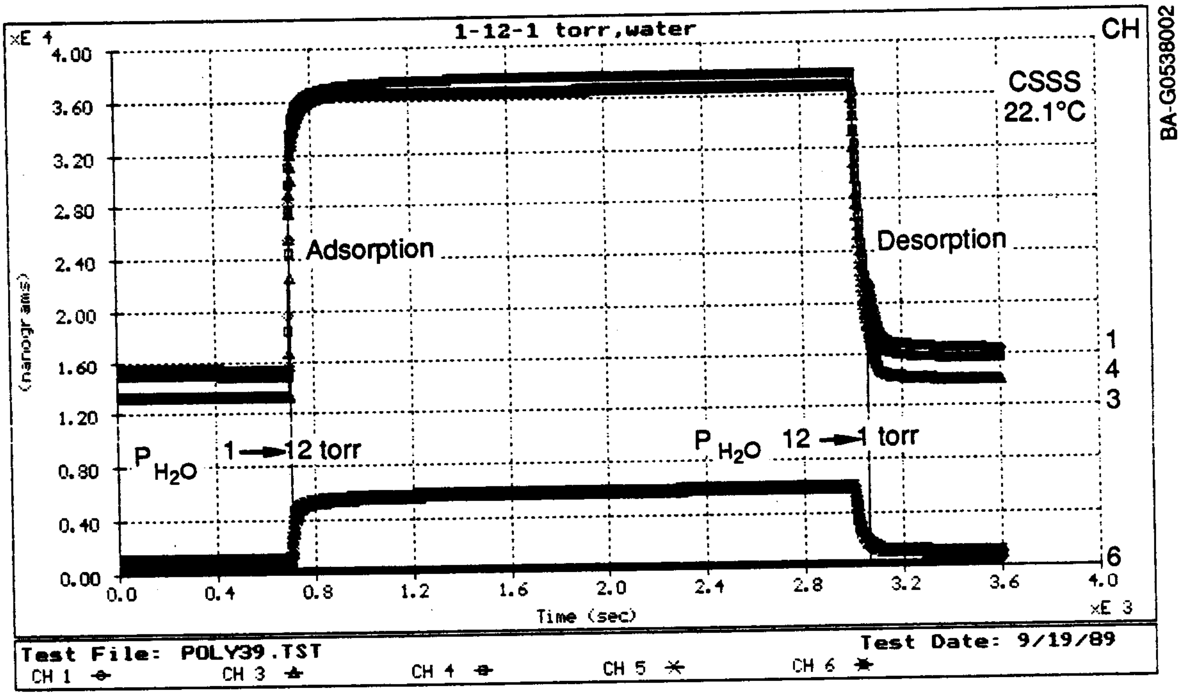

Figure 4-14. The mass change versus time at 22.1°C of four different samples of CSSS after an increase in water vapor pressure from 1 to 12 torr and a decrease back to 1 torr, as obtained with the DAQS.

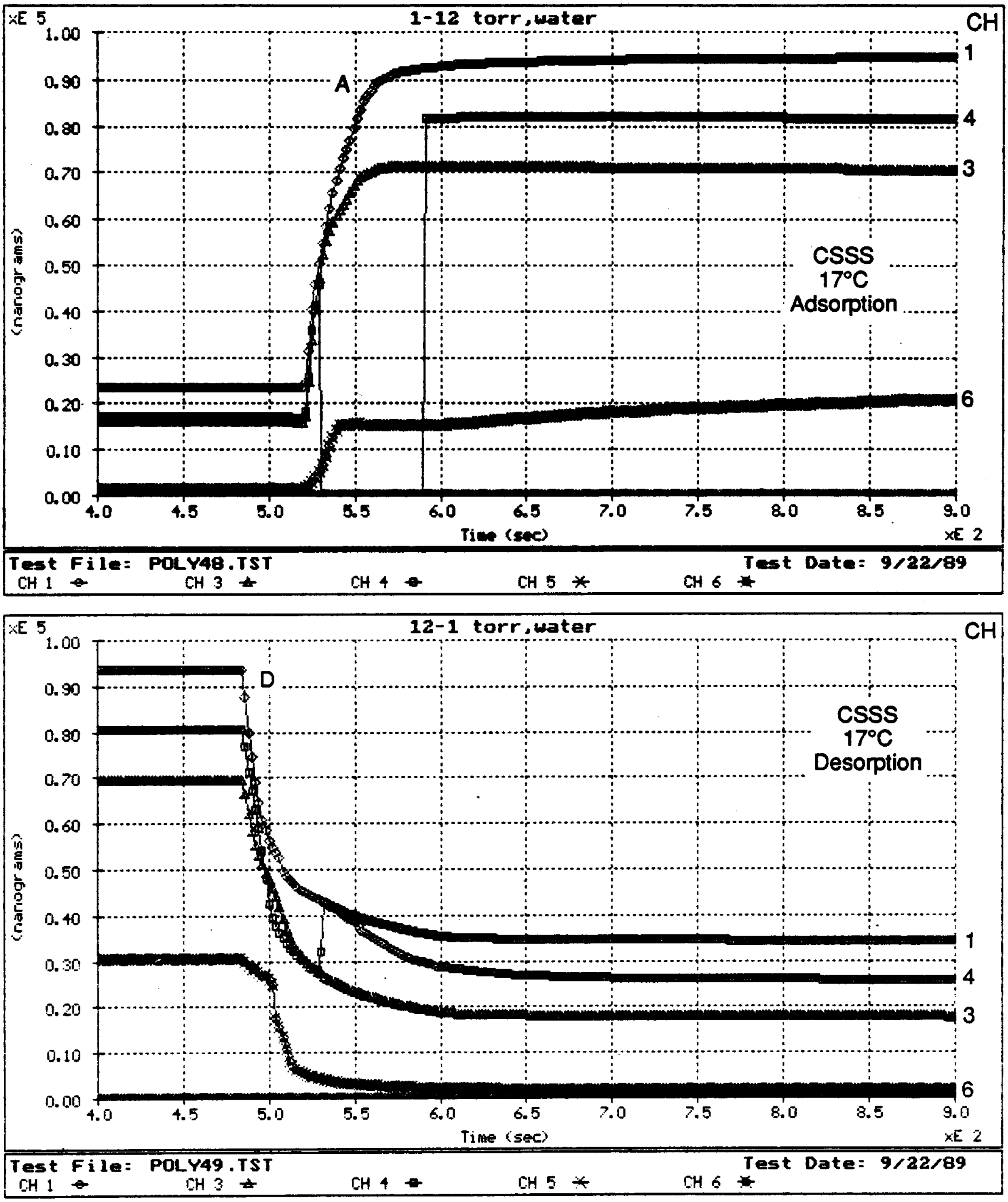

Figure 4-15. The mass change versus time at 17°C of CSSS after an increase in water vapor pressure from 1 to 12 torr and a decrease back to 1 torr, as obtained with the DAQS.

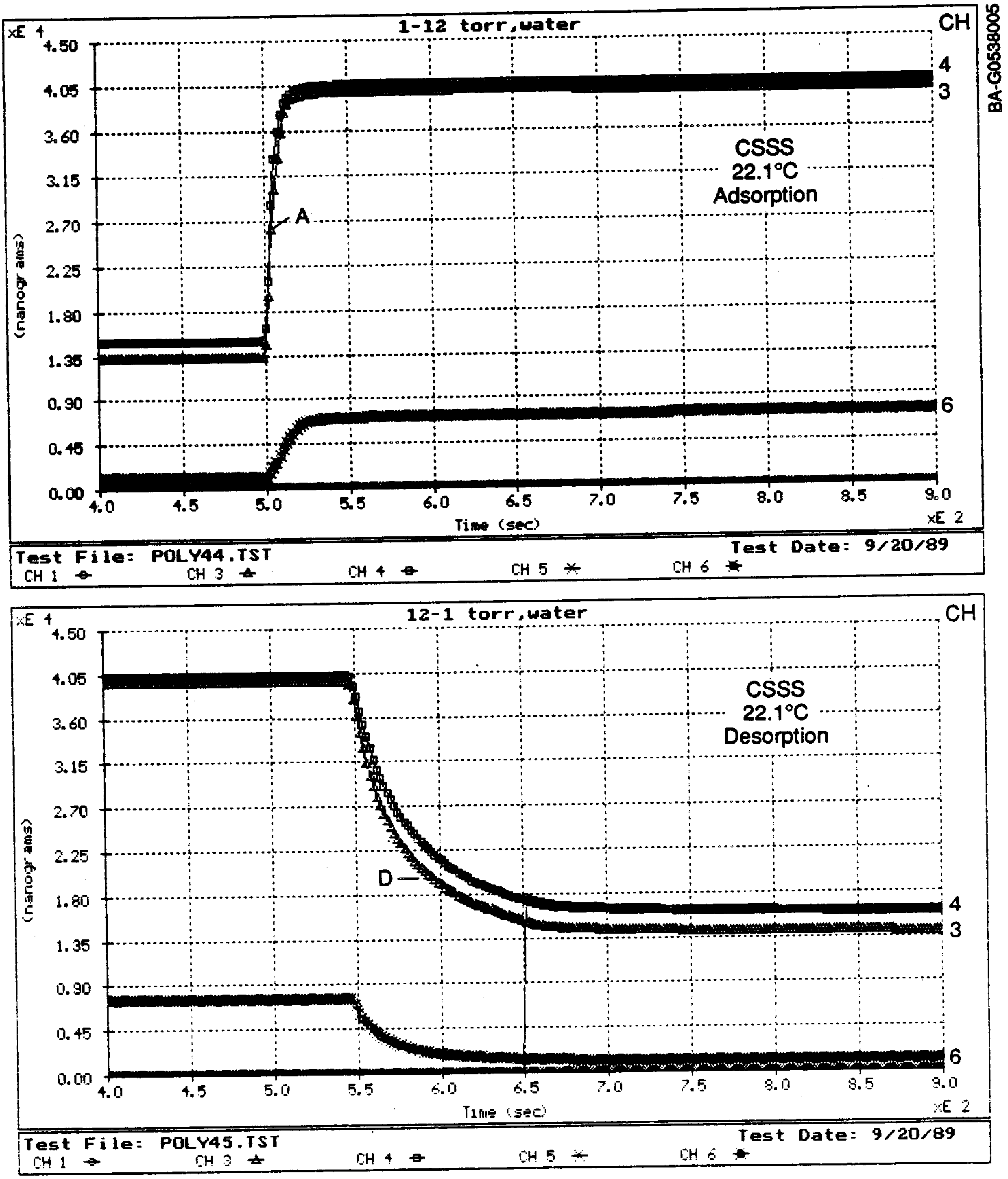

Figure 4-16. The mass change versus time at 22.1°C of CSSS after an increase in water vapor pessure from 1 to 12 torr and a decrease back to 1 torr, as obtained with the DAQS.

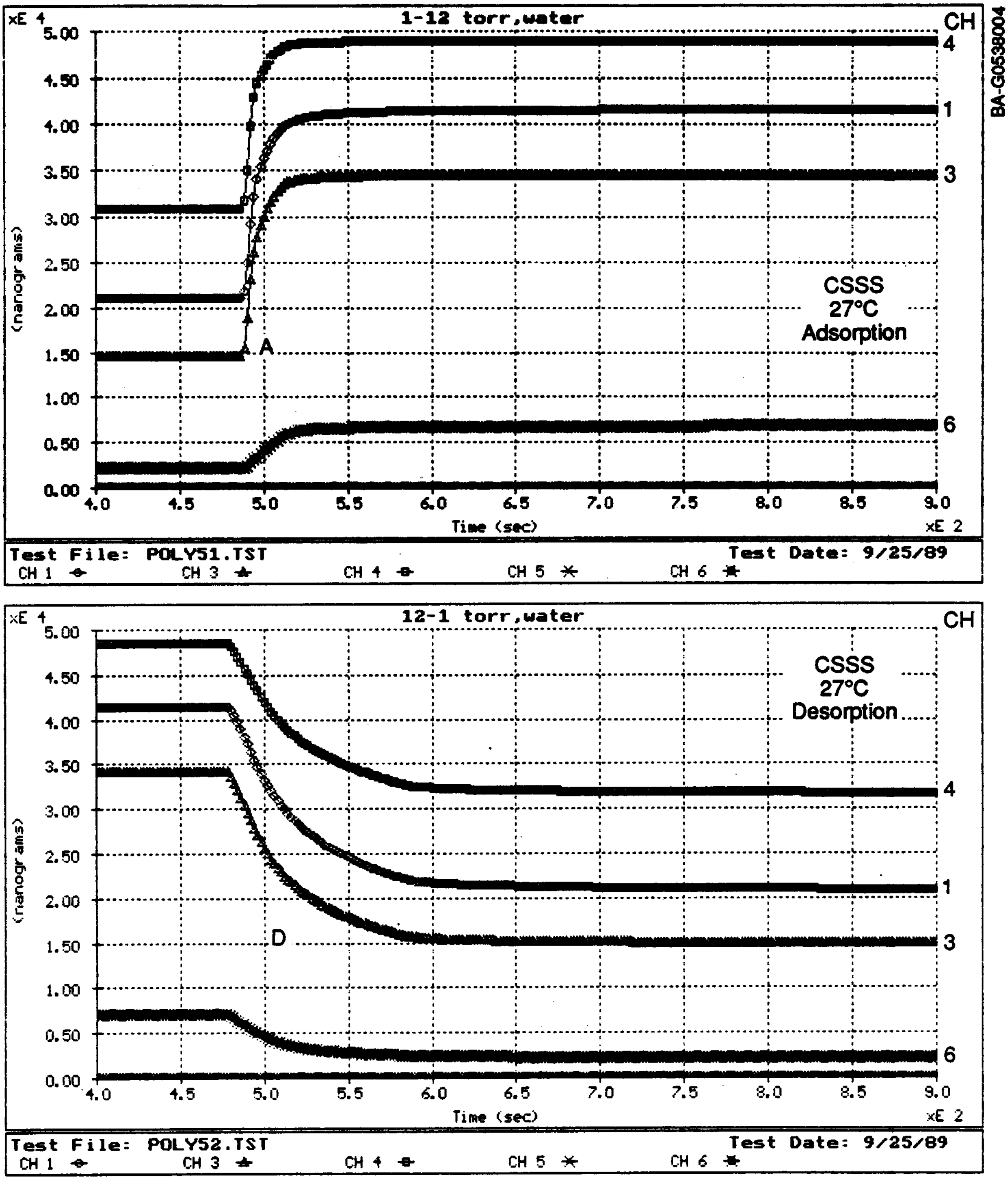

Figure 4-17. The mass change versus time at 27°C of CSSS after an increase in water vapor pressure from 1 to 12 torr and a decrease back to 1 torr, as obtained with the DAQS.

Table 4-1. Approximate Time in Seconds to Reach 90% and 100% of the Total Mass Change of CSSS for Water Vapor Pressure Changes from 1 to 12 to 1 torr at 17°, 22.1°, and 27°C

	Adsorption (1 to 12 torr)		Desorption (12 to 1 torr)	
	90% ΔM	100% ΔM	90% ΔM	100% ΔM
17°C	35	170	90	215
22.1°C	15	100	70	200
27°C	20	80	80	190

5.0 OTHER RELATED ACTIVITIES

5.1 Collaboration with Cargocaire Engineering Co., Inc.

Interactions were maintained with Cargocaire during 1989 and included a visit by A. W. Czanderna at the Amesbury, Massachusetts, facility in June. Two important requests were made by S. Brickley of Cargocaire: (1) to obtain sorption data at approximately 62°F and (2) to secure kinetic data for rapid changes between 5% and 60% R.H. Both requests were already in our planned effort. The isotherms obtained at 17°C fulfilled Cargocaire's first request, and the kinetic data presented in Section 4.6 fulfilled its second request. In addition, the encouraging results obtained with VERSA TL 73 (PSSALS) were communicated to Cargocaire personnel during the site visit, and they were urged to consider some exploratory experiments using PSSALS.

5.2 ASHRAE Paper

A paper on prior work on this task was prepared for publication in the ASHRAE proceedings and presentation at the ASHRAE meeting in Vancouver, B.C., Canada, June 25-28, 1989. The printed version of the paper is attached as Appendix I. A summary of the current status of this task was also presented in Vancouver at a review of the DOE Solar Cooling Program on June 26.

5.3 Patent Application

Information was supplied on September 5, 1989, to SERI's patent counsel in response to comments by a patent examiner for the patent application by A. W. Czanderna, inventor, entitled, Desiccant Composition for Desiccant Cooling Systems. The patent application was resubmitted on October 27, 1989, following interactions between A. W. Czanderna and legal counsel.

5.4 Equipment Problems

Approximately 10 weeks of data collection were lost to the project between January and March 1989 because of a defective turbo pump and power supply and five separate defective replacement parts supplied by Balzers. The details of the problem and the possible solutions were documented and attached to the March 1989 monthly report. This documentation is available on request from A. W. Czanderna.

5.5 Personnel: Polymer Scientists

A resident polymer scientist is the best solution for meeting the task needs for polymer synthesis and modification. During 1988, postdoctoral researcher P. Gomez fulfilled this need until he accepted an industrial staff position. For the rest of 1988, H. Neidlinger supervised a resident technician and part-time personnel to satisfy the task needs as a stop-gap measure. Three postdoctoral polymer scientists were interviewed in 1988 and January 1989 to replace Gomez. All three candidates were acceptable to the technical staff, but SERI management did not pursue making an offer because of their citizenship status. When Neidlinger accepted a post at an industrial firm in April 1989, the task was left without a resident polymer scientist. As a result, the statement of work (Appendix H) was prepared in May, a subcontract was authorized on August 1 to Eastman Kodak, and a period of performance was initiated on October 17.

About 30 applicants responded to a national search for a full-time polymer scientist; two interviews were conducted in September. One of these applicants accepted SERI's offer to serve as a postdoctoral researcher as a polymer scientist but could not be added to our staff because the appropriate forms for employment of non-U.S. citizens were not approved by DOE. When sufficient funds become available on the ADM part of SERI's desiccant task, a newly recruited polymer scientist may be available for the molecular engineering of new and modified polymers.

6.0 CONCLUSIONS

The conclusions reached in 1989 from the characterization studies are as follows:

- From isotherms determined for PSSA, PSSALS, PSSASS (several sources), and PSSAKS, the optimum material is PSSALS based on isotherm shape, capacity, adsorption and desorption kinetics, and stability. In order of decreasing suitability, the shape and capacity are PSSA > PSSALS ≈ PSSASS > PSSAKS, which is inversely related to an increasing counterion size (i.e., $H^+ < Li^+ < Na^+ < K^+$). The performance loss and acidic character of PSSA probably preclude its use as an ADM for CDCS.
- The adsorption and desorption kinetics for all the ionic salts of PSSA studied (PSSALS, PSSASS, PSSAKS, AND PSSAAS) may be fast enough for use in a CDCS with a wheel rotation speed of 6 min per revolution. More than 90% of the capacity change for adsorption and desorption at 22.1°C occurs in 3 min or less for samples 3 to 5 µm thick. Whether the capacity change is still large enough and fast enough in an engineering configuration needs to be verified.
- Wide variations in the sorption capacity for different sources of PSSASS indicate careful control of the preparation procedure is required for obtaining an optimum isotherm shape and capacity.
- The sorption capacity and isotherm shape of PSSA depend on the time from preparation, the capacity decreases by as much as a factor of 200 in 5 months, and the isotherm shape changes from Type 2 to sigmoidal and back to Type 2.
- The isotherm shape for PSSA retained in a dichloroethane solution is not favorable as a desiccant in DCS applications.
- The PSSAAS studied is probably not suitable as an ADM for CDCS applications because it exhibits a large hysteresis between adsorption and desorption.
- CSSS isotherms from material supplied by Aldrich Chemical are comparable in shape, capacity, and stability to those from Scientific Polymer Products, Inc.
- Isotherms obtained at 17°, 22.1°, and 27°C exhibit an unexpected behavior for PSSALS, PSSASS, and SPSS. The largest capacity is obtained at 22.1°C.
- The sorption kinetics for CSSS are faster than for the ionic salts of PSSA. More than 90% of the capacity change for adsorption and desorption occurs in 100 to 125 s for temperatures of 17°, 22.1°, and 27°C.
- The time required for the adsorption or desorption step appears to be slightly temperature dependent, with the slowest times occurring at 17°C.
- Differences in the sorption rates for thicknesses between 1 and 10 µm of PSSASS and CSSS are not great enough to be detected with our current procedures (Appendix F). This is a remarkable result that means water diffuses rapidly through these polymers.
- Polymeric samples thicker than 12 to 15 µm have not been successfully studied using the QCM technique.
- The new DAQS is a significant improvement for the QCM apparatus, especially for monitoring the kinetics of adsorption and desorption. It will also be

of great value for studying the cyclic stability of polymeric desiccants, even though this has not yet been demonstrated.

- Further work is needed to understand the unexpected temperature dependence of isotherms and to determine the optimum adsorption temperature. This additional work is required before heats of adsorption can be determined.
- Further work is needed to understand the time-dependent performance degradation of PSSA, but this does not appear important for CDCS applications at this time.
- Further work is needed to identify the optimum regeneration temperature, especially because Type 2 isotherms obtained at 17° and 22.1°C tend to become Type 3 isotherms at 27°C. The initial findings are extremely favorable for using polymeric materials in CDCSs.

7.0 FUTURE ACTIVITIES

As given in Appendix D, the long-term technical approach for studying the water vapor sorption by ADMs for use in regenerative DCSs, includes conducting experimental work and interpreting the data to secure the necessary understanding. The following parts of the technical approach are particularly relevant for 1990.

1. Identify, select, rank, and prepare for study of potential ADMs.
2. Determine the effect of chemical modification of candidate ADMs on the sorption performance.
3. Modify polymeric materials to improve their sorption performance and synthesize new polymeric materials that are molecularly engineered to function as an "ideal" ADM.

For point 1, the literature search will be updated periodically. Any polymers identified as potential candidates must be screened for their suitability as candidate ADMs in the same manner as those discussed in Section 4.0. For point 2, chemical modification of candidate polymers will be continued with the objective of improving the isotherm shape and sorption capacity without compromising the other desirable polymer properties. For point 3, additional efforts to synthesize and modify polymeric materials, with the objective of making an "ideal" ADM, will be made. Both 2 and 3 require that additional personnel with polymer synthesis experience be added to the project.

The objectives for the ADM subtask during FY 1989 and later years, where the numbers in parentheses correspond to those in the technical approach, are to

1. Modify optimal commercially available or prepared co-polymers with small and large counterions (2, 8)
2. Synthesize new, cross-linked, hydrophilic desiccant polymers (2)
3. Investigate the potential of thermal- or light-triggered collapse phenomena of super hydrophilic polymers (2)
4. Characterize all polymers prepared for their essential physical properties and functional group concentrations (6)
5. Characterize the water sorption performance properties for all polymers prepared (6)
6. Investigate the isotherm shape at sorption temperatures between 15° and 35°C (6) and at about 80°C
7. Further investigate the puzzling results obtained in 1989.

Items (11) and (12) in Appendix D will be continued, as needed, to complement the new work performed in (1) through (7).

Major anticipated benefits that will accrue from work in FY 1990 and beyond include (1) identifying ADMs that have the properties of or approach the ideal desiccant; (2) evaluating several ADMs in an engineering configuration through interactions with other projects funded by DOE, the Gas Research Institute, and private industry; and (3) establishing SERI as a primary center of quality assurance for characterizing the sorption performance of both inorganic and organic materials, independent of an engineering configuration. Characterization work on other SERI tasks could then reveal the sorption performance in an engineering configuration.

Depending on the funding levels, the work may also provide required information for items (7) through (10) in the technical approach, i.e., systematically modifying inorganic materials and characterizing them for sorption performance; studying the cyclic stability of candidate polymers after concluding initial sorption screening, where real-time cyclic stability studies will be made to provide accelerated simulation of real-time use in a DCS; determining heats of adsorption for candidate materials; performing theory and computer simulation for diffusivity measurements for the geometry of a polymer on a QC or as a suspended film and comparing predictions with actual measurements; performing controlled studies to identify causes of sorption degradation induced by contaminants (e.g., silica gel and sorption, composition, and bonding); and initiating studies to understand basic vapor-surface interactions between water and two or three candidate materials (sorption, bonding, surface composition, pore size, etc.).

The following activities are planned for FY 1990:

1. Characterize the sorption performance of laboratory-prepared polymers with different cations prepared by Eastman Kodak under controlled conditions.

2. Characterize the sorption performance of one new hydrophilic desiccant polymer.

3. Complete a progress report.

The sorption performance properties of the new and potentially "ideal" polymeric desiccants will be measured with the QCM.

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APPENDIX A

PROJECT SUMMARY (1985-1989)

A.1 Research Scope

A.1.1 Background

An advanced desiccant material (ADM) can advance solar buildings technology not only by lowering the cost of commercial solid desiccant cooling systems (DCSs) to compete with conventional air conditioning but also by eliminating the need for electric utilities to add peak-load generating capacity.

The optimum sorption properties of the desiccant materials in DCSs were identified in a recent study of systems analysis (Collier, Cale, and Lavan 1986). If an ideal desiccant can be identified, the coefficient of performance (COP) of a DCS can be improved from 0.85 to 1.05, which can now be obtained with silica gel, the current industrial standard, to 1.3 to 1.4, or closer to the theoretical maximum of about 2.5. The COP is equal to the cooling capacity divided by the heat input (Collier, Barlow, and Arnold 1982). At the same time, the cubic feet per minute per ton can be reduced from a range of 310 to 400 for silica gel to a range of 200 to 250 for an ideal desiccant. If both of these factors are achieved, DCS could be cost competitive with other current air conditioning systems; this is not possible for silica gel (Collier, Cale, and Lavan 1986). Prior to the conclusions of Collier, Cale, and Lavan, this project was initiated to identify new, low-cost, next-generation materials with the desired water vapor sorption performance, i.e., isotherm shape, sorption capacity, adsorption and desorption kinetics, and cyclic stability. Of the commercially available inorganic (e.g., alumina gel, chromia gel, charcoal) and organic materials, more than 25 commercially available polymeric materials have been selected as potential candidates for use in DCSs. By considering the available polymeric desiccants, scientists note or have demonstrated that

- Polymers have the potential of being modified so that sorption isotherms of the desired shape and heats of adsorption of approximately 10.8 kcal/mol are obtained.
- Polymers have been identified that sorb water from 5% to more than 80% of their own weight.
- Polymers have the potential for being readily fabricated into shapes for DCSs, e.g., a honeycomb structure 10 × 0.04 × 0.06 in.; when a desiccant polymer cannot be a structural material, it may be grafted onto a structural polymer.
- Polymer structures have the potential of being fabricated to provide high diffusivities of water vapor through the material, permitting sorption and desorption to be completed within a few minutes.
- Polymers can be regenerated at temperatures below 80°C for thermally desorbing water.
- Polymers have the potential for maintaining long-term stability through thousands of sorption-desorption cycles.

- Commercial polymers are available at less than \$1/lb, comparable to the cost of commercial-grade silica gel.

Accordingly, polymeric materials could not only serve as both the desiccant and support structure in a desiccant wheel but could also be easily and inexpensively replaced if their water sorption capacity degrades with time. Thus, the initial emphasis of this research has been to characterize the water sorption performance of polymeric materials that could serve in an economically competitive DCS.

A.1.2 Statement of Work

DOE has an interest in identifying next-generation, low-cost materials as advanced desiccants for solar cooling applications and to understand the role of surface phenomena on the performance of ADMs. Research in this area may lead to new or modified materials that will improve the COP of DCSs and provide a scientific understanding of the water vapor-desiccant interactions to underpin the technological application of durable ADMs. To accomplish the objectives of this research, SERI will

1. Identify, select, prioritize, and prepare for a study of potential ADMs
2. Modify polymers or inorganic materials to improve their sorption performance and synthesize new polymeric materials that are molecularly engineered to function as an "ideal" ADM
3. Identify the performance criteria of ADMs, including sorption performance and durability
4. Identify the necessary measurements for characterizing the water-vapor sorption performance of potential ADMs
5. Design, purchase, construct, install, and use the experimental apparatus necessary for characterizing the sorption performance and establishing the durability of ADMs
6. Measure the sorption performance and determine relevant physical parameters of potential ADMs to establish which materials are candidate ADMs based on the criteria in point 3.
7. Determine the repeatability of the sorption performance of candidate ADMs from points 1, 2, 3, 4, and 6 as a function of sorption-desorption cycles at time intervals corresponding to DCSs
8. Determine the effect of chemical modification of ADMs and their surfaces on sorption performance
9. Conduct fundamental scientific investigations to understand the interplay among composition, bonding, topography, surface area, pore volume, pore size distribution, morphology, and their changes during cycling and use in real environments
10. Perform analytic and theoretical work, as needed, to assess the opportunities and limitations of candidate ADMs for use in the engineering configurations of contemporary DCSs
11. Cooperate with others performing desiccant R&D to expedite the testing of candidate ADMs in engineering configurations

12. Prepare reports, publications, and make presentations to disseminate the results of the work.

A.1.3 Objectives/Research Progress

A.1.3.1 Objectives

The technological objective is to identify a next-generation, low-cost material with which solar radiation or heat from another low-cost energy source can be used for regenerating the water vapor sorption activity of the desiccant. The scientific objective of this task is to determine how the desired sorption performance of ADMs can be predicted by understanding the role of their surface phenomena and the materials modifications.

A.1.3.2 Research Progress

Referring to the numbered items in Section A.1.2 with the numbers at the left margin, and to references by parentheses 1 to 6 in the Bibliography (Appendix A.2.3), we performed the following tasks:

1a. Completed a literature search (1), identified polymeric and inorganic materials as potential advanced desiccants (1), prioritized them for study (1), and prepared them for characterizing their sorption performance (1,3,5).

1b. Developed in detail the opportunities for using polymeric materials as ADMs (2,3).

2. Established the feasibility for synthesizing and modifying polymers as ADMs (6).

3a. Identified the key materials parameters for prioritizing potential ADMs (1), and ranked all identified materials (more than 300 possibilities) (1).

3b. Identified the water vapor sorption performance criteria for narrowing the potential ADMs to a few candidate ADMs (5). The sorption performance includes the sorption capacity from 5% to 60% R.H., isotherm shape, rate of adsorption and desorption, and cyclic stability of the ADM in water vapor.

4. Identified microgravimetric, compositional surface analytic, infrared spectroscopic, scanning electron microscopic, and thermal gravimetric measurements as the minimum number of techniques necessary for studying desiccant materials and understanding their morphological and surface properties (1).

5. Designed, purchased, assembled, constructed, installed, and used a quartz crystal microbalance (QCM) for characterizing the sorption performance of organic (polymeric) and inorganic materials (3,4,5) and designed, assembled, and installed a Sartorius microbalance system for use on the project (5,6).

6a. Measured the sorption performance of more than 23 potential commercially available polymeric ADMs with the QCM (1-5) and used the criteria in point 2 to narrow the number to seven candidate ADMs (5). The measurements include sorption isotherms, rate of adsorption and desorption at each pressure increment or decrement, cyclic stability, and qualitative evaluations of permeation rates (3-5). Measurements of the heat of adsorption, pore volume, morphology, etc., for more detailed materials characterization have not been made.

6b. Measured the sorption isotherms for commercially available polystyrene sulfonic acid sodium salt (PSSASS) and sodium polystyrene sulfonate (SPSS) for various molecular weights and for SERI-prepared modifications of polystyrene sulfonic acid (PSSA) and PSSASS with various molecular weights and degrees of sulfonation (6). Measured the sorption isotherms for commercially available cationic salts of PSSA (7).

6c. Designed an experimental procedure with an existing thermal gravimetric apparatus for studying the cyclic stability of ADMs in humid air.

6d. Demonstrated that surface compositional analysis using x-ray photoelectron spectroscopy and infrared spectroscopy will be useful for securing fundamental and technological information about both current and advanced desiccant materials.

7. Initiated cyclic stability studies of several candidate polymeric ADMs and established that nine polymers remain as serious candidate ADMs (5).

8. Prepared proposals for securing the funding necessary to pursue the other issues (2-11) in the statement of work that have not been addressed or are only partly completed.

A.2 Research History

A.2.1 Funding Levels for ADM Research (in $K)

	FY 1985	FY 1986	FY 1987	FY 1988	FY 1989	TOTAL
Operating	80	75	150	126	86	517
Capital	55	None	None	None	None	55
TOTAL	135	75	150	126	86	572

A.2.2 Technical Problems and Solutions Achieved or Planned

The planned solutions are identified under future directions. From hundreds of potential commercially available polymeric desiccants, we narrowed the number of candidate ADMs to seven. A crucial problem for the future will be to synthesize polymeric materials with the properties tailored to the needs of an ADM. This has never been done but should be realizable with the continued effort of a polymer scientist and continued characterization work. Clearly, there is a need for sorption performance characterization of ADMs using beam microbalance techniques. At the same time, the capital investment in SERI's QCM has resulted in a unique apparatus that is now being copied by a number of industrial research laboratories (publication 4).

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A.3 Future Direction

The long-term technical approach for studying the water vapor sorption by ADMs for use in regenerative DCSs consists of carrying out experimental work and interpreting the data to secure the necessary understanding. The following variables are particularly relevant: (1) selection, preparation, and study of a particular material; (2) water vapor sorption capacity and heat of adsorption by the solid desiccant; (3) rate of adsorption at ca. 22°C and desorption at a modestly elevated T; (4) repeatability of points 2 and 3 as a function of cycles with short time intervals; (5) effect of chemical modification of the desiccant on points 2, 3, and 4; and (6) changes in the composition and topography of desiccant surfaces and the bonding of water vapor during cycling.

For pursuing the statement of work, we plan to continue using a QCM and initiate using a Sartorius microbalance system to obtain the water sorption data required for points 1 to 4. Specifically, we need to (a) systematically modify or synthesize polymers and characterize them for sorption performance, (b) continue sorption screening of polymers modified at SERI, (c) initiate using a Sartorius microbalance system to screen candidate polymers that cannot be studied with the QCM, (d) characterize the sorption performance of SERI-synthesized polymers, (e) complete the final sorption screening of nine candidate commercially available polymers, (f) complete the final sorption screening of as many as eight potential candidate commercially available polymers, (g) study the cyclic stability of candidate polymers after concluding initial sorption screening, where real-time cyclic stability studies will be made to provide accelerated simulation of real-time use in DCSs, (h) systematically modify inorganic materials and characterize them for sorption performance, (i) determine heats of adsorption for candidate materials, (j) complete our efforts on a technique for studying inorganic powders (e.g., silica gel) with the QCM, (k) study inorganic materials and some polymers using the Sartorius microbalance system, (l) perform theory and computer simulation for diffusivity measurements for the geometry of a polymer on a quartz crystal (QC) and compare prediction with actual measurements, (m) perform controlled studies to identify causes of sorption degradation induced by contaminants (e.g., silica gel and sorption, composition, and bonding), and (n) initiate studies to understand basic vapor-surface interactions between water and two or three candidate materials (sorption, bonding, surface composition, pore size, etc.).

The addition of (c) and (k) is especially attractive because SERI will have the means to act as a center of quality assurance for characterizing the sorption performance of both inorganic and organic materials, independent of an engineering configuration. Characterization work on other SERI tasks could then reveal the sorption performance in an engineering configuration.

APPENDIX B

ADVANCED DESICCANT MATERIALS AND DESICCANT COOLING SYSTEMS: RELATIONSHIP AND BACKGROUND

B.1 DCSs

Systems with solid desiccants are currently used in industrial air-drying applications (Solar King 1984) and in DCSs. These use a desiccant-laden wheel in which air may flow in the axial direction only. The solid desiccant (typically, silica gel or lithium chloride) is mounted onto a wheel, and the air to be dried flows through one side of the wheel; the desiccant on the other side of the wheel is simultaneously being dried by an externally heated air stream. These two air streams are kept physically separated to maintain the distinctly separate functions of air dehumidification and desiccant regeneration. The historical development that led to current commercial systems was summarized by Collier, Barlow, and Arnold (1982).

The commercial systems are primarily intended for specialized applications that require dehumidifying air and usually do not produce a significant net cooling. There are important differences in design philosophy between solar-regenerated DCSs and commercial desiccant dehumidifiers. The most important difference involves the thermal and electrical COPs. The COP was discussed and defined by Collier, Barlow, and Arnold (1982). For many years, commercial desiccant dehumidifier manufacturers have chosen markets in which vapor-compression equipment cannot compete, i.e., applications where extremely dry air is required or where latent cooling loads are high. The energy requirements to achieve these conditions have not been a major concern, and as a consequence, the desiccant dehumidifiers often have very low thermal and electrical COPs. Recently, dehumidifier manufacturers, who have been funded by the Gas Research Institute (GRI) entered the supermarket heating, ventilating, and air conditioning (HVAC) business where prospects appear attractive.

B.2 Relationship of Desiccant Materials to Desiccant Cooling Systems

Desiccant materials must have a favorable performance/cost ratio, provide satisfactory performance, and have cost-effective lifetimes; widely available materials need to be certified, modified, or, in some cases, developed specifically for use in DCSs. Some of the important parameters for the water-solid desiccant material system include isotherm shape, sorption capacity, heat of sorption, rate of sorption at or near the desiccant bed temperature (~25° to 55°C), rate of desorption at an elevated temperature, physical and chemical stability of the desiccant, and cyclic repeatability of the sorption amount and rates. Some important conclusions and recommendations on these parameters were reached in the recent modeling study for regeneration at 160°C (Collier, Cale, and Lavan 1986), but the possibility of identifying new materials with optimal properties was not considered.

Silica gel and lithium chloride are now the most widely used desiccant materials in DCS wheel geometries. Extensive optimization studies of the engineering design of DCS units have been carried out using silica gel (Barlow 1982; Jurinak 1982; Pesaran and Mills 1984; Schlepp and Schultz 1984; Pesaran et al. 1986). Models in systems analysis studies for estimating the achievable thermal and electrical COP also use the properties of silica gel because they have been documented extensively over several decades (Parent 1985). Because the water sorption properties of the desiccant are crucial to the performance of any system, this desiccant materials research effort was initiated to search for and measure the properties of materials that could not only be better desiccants than silica gel but could also approach the "ideal" desiccant material in its sorption performance. In addition, manufacturing methods with new materials could have a profound impact on reducing the dehumidifier cost.

Except for recent work on this project and on manganese oxides (Fraioli 1983), most of the published work in the past decade has been on silica gels and zeolites. These materials have performance limitations (e.g., isotherm shape, large heat of adsorption, high regeneration temperatures, and hysteresis on cycling) that restrict their potential for use in DCSs (Collier, Barlow, and Arnold 1982; Collier, Cale, and Lavan 1986). Therefore, an ADM is a natural research need for enhancing the potential of cost-effective DCSs. These results led GRI to initiate a multi-year desiccant materials research program in 1986; in 1987, it began supporting work on hydrate-type inorganic materials at LaRoche Chemicals Inc., proprietary organic formulations at the Eaton Corporation as well as on other cooperative efforts. No publications of the GRI-supported work appear in the open literature.

B.3 Polymers as ADMs

The relationship of desiccant materials to DCSs and background information about studies of ADMs are discussed in Appendix B.2.

From a literature search (Czanderna and Thomas 1986), we identified both inorganic and organic (i.e., polymeric) materials as potential candidate ADMs for use in DCSs. To focus our research, we initially selected 21 commercially available polymeric materials for further study. These were listed in previous reports (Czanderna and Thomas 1986; Czanderna 1988, Appendixes A and B). The process used to narrow the list of more than 300 commercially available polymers was also reported (Czanderna and Thomas 1989, Section 3.0). We identified several additional polymers as our studies progressed.

By considering the available polymeric desiccants, we were able to note the following:

- Polymers have the potential of being modified so that sorption isotherms of both the desired shape and heats of adsorption of approximately 10.8 kcal/mol are obtained.
- Polymers have been identified that sorb water from 5% to more than 80% of their own weight and have the potential of sorbing 10,000% of their own weight.
- Polymers have the potential for being readily fabricated into shapes required for DCSs, e.g., a honeycomb structure 10 × 0.04 × 0.06 in.; when a desiccant polymer is not a structural material, it may be grafted onto a structural polymer.

- Polymer structures have the potential of being synthesized to provide high diffusivities of water vapor through the material.
- Polymers have the potential for being regenerated at temperatures below 80°C for thermally desorbing water.
- Polymers have the potential for maintaining long-term stability through thousands of sorption-desorption cycles.
- Commercial polymers are available at less than $2/lb, comparable to the cost of commercial-grade silica gel.

Accordingly, polymeric materials could not only serve as both the desiccant and the support structure in a desiccant wheel but also could be easily and inexpensively replaced if their water sorption capacity degrades. The initial need of this research was to characterize the water sorption performance of polymeric materials that could serve in an economically competitive DCS. The current and future needs include modifying candidate polymeric materials identified in prior work and synthesizing new polymeric materials that have the desired water vapor sorption performance properties.

The key technical questions in seeking candidate polymers for DCSs are the following:

- Will any commercially available polymer have the properties required for use in a DCS? Several promising candidate materials have been identified, but none have optimum or "ideal" properties.
- Can the polymeric material be modified to improve performance properties such as isotherm shape, heat of adsorption, regeneration temperature, cyclic stability, and diffusivity? The authors are convinced that this question will be answered affirmatively, and recent progress in making modified PSSASS to support our conviction is the main content of this report.
- If commercially available polymers are not suitable, can laboratory-prepared polymers be synthesized with suitable sorption, desorption, and stability properties?
- Do the performance properties depend on the sample size and configuration, e.g., 0.1 mg (QCM), 100 mg (beam microbalance), and SERI test-loop scale and configuration?
- What impurities in the air stream result in a loss of sorption performance of candidate polymers?
- Are there other degradation processes that cause a candidate polymer to lose sorption performance?

B.4 Background for ADM Studies

The arguments for desiccating water from air in an open-cycle DCS are well known (Collier, Barlow, and Arnold 1982). The principal limitations are related to finding a desiccant material with the required combination of sorption parameters, such as capacity, sorption heat, sorption rates at the bed temperature, desorption rate at a minimally elevated temperature, and cyclic stability. Other parameters or properties of interest have been identified (Czanderna and Thomas 1986). These sorption parameters are connected with the energetics associated with gas-solid interactions (Gregg and Sing 1982; Czanderna and Vasofsky 1982).

A number of inorganic porous solids available have large internal surface areas and pore volume with an enormous affinity to sorb water. Some types of inorganic solids may sorb as much as 40% of their weight and remain physically dry (Gregg and Sing 1982), which is desirable for DCS applications (Collier, Barlow, and Arnold 1982). Some organic polymers may sorb more than 50% of their weight (Bulygin et al. 1983; Czanderna and Thomas 1986); the uptake of water here is internal to the polymer, and as with many porous solids, the dynamics of the sorption process is diffusion controlled.

The sorption of water vapor by the desiccant is given by the reaction scheme

$$D(s) + H_2O(v) \longrightarrow D_+H_2O_{surface} \qquad \text{(B-1)}$$

and

$$D(s) + D_+H_2O_{surface} \longrightarrow D_+H_2O_{internal} + D(s)\ , \qquad \text{(B-2)}$$

where D(s) is a solid desiccant adsorption site. Water vapor adsorbs onto the surface (Eq. B-1) and permeates into the solid by several possible diffusion processes (Eq. B-2) to provide the total sorption. Empty surface sites are filled by further adsorption (Eq. B-1). Desorption of water vapor from the desiccant occurs by the reverse sequence

$$D_+H_2O_{surface} \longrightarrow D(s) + H_2O(v) \qquad \text{(B-3)}$$

and

$$D(s)_{surface}{}^{+D} + H_2O_{internal} \longrightarrow D_+H_2O_{surface} + D(s)_{internal}\ , \qquad \text{(B-4)}$$

where empty surface sites are generated (Eq. B-3) by desorption, and water sorbed in the material must first occupy a surface site (Eq. B-4) before desorpion via Eq. B-3.

Although the details of the molecular processes are much more complex than illustrated by Eqs. B-1 through B-4, they illustrate that the sorption capacity is gained by at least two kinetic steps involving the rate of adsorption (Eq. B-1) and the rate of permeation into the solid (Eq. B-2). Equations B-3 and B-4 illustrate the reverse steps of desorption and diffusion. The adsorption and desorption rates are usually much faster than the permeation and diffusion rates. The permeation (diffusion) steps provide the solid-side resistance in the sorption-regeneration sequence. The principal limitations are related to finding a desiccant material with the required combination of isotherm shape, sorption capacity, sorption heat, sorption rates at the bed temperature, desorption rate at a minimally elevated temperature, cyclic stability of the sorption properties, and stability of the desiccant itself. These parameters are connected with the energetics and kinetics associated with gas-solid interactions.

The forces primarily responsible for the sorption processes arise from interactions of the electric field at the surface of the solid-adsorbate molecules, which is water for solid desiccants. Because of its large dipole moment and polarizability, the water molecule produces a large heat of adsorption. The total interaction between the water molecules and the adsorbent surface contains contributions from several types of interactions, such as dipole-dipole, dipole-quadrupole, and dipole-induced dipole. Because water is a polar molecule and the sorption sites are primarily ionic, it appears conceivable that the electric field at the surface could be modified by introducing different ions or functional groups at the surface, changing the heat of adsorption. On inorganic surfaces, modifications could be done by ion-exchange techniques and during the preparation of organic materials. The modifications can also influence the sorption capacity and isotherm shape, so the desired material must have the optimal combination of capacity and adsorbate-binding energy.

From sorption isotherms, the binding energy of the water adsorbate to the solid can be determined. The rate of diffusion through the porous material can be calculated, and in principle, the rate of desorption from the solid can be determined and compared with experimental results. The comparison must be made using materials that at least approach the configurations used for the calculations. Practically, the sorption rate processes will be reduced by pore volume diffusion and intraparticle diffusion in a packed bed of particles. Although some sorption data are available in the literature (Gregg and Sing 1982) for candidate desiccant adsorbent materials, these data have not been analytically scrutinized to determine the suitability of new materials in advanced desiccant applications.

Recent articles show experimental activity in water vapor adsorbent systems and in the analysis of the associated phenomena (Czanderna and Thomas 1986). In most of these studies, the conventional volumetric, scanning electron microscopic, and electron microscopic techniques used provide only a limited understanding of the fundamental processes. Surface compositional analyses of solids have not been correlated with changes in sorption behavior. Bonding information available from infrared spectroscopy has been coupled with adsorbed amounts by authors of only a few papers. The QCM has not been used extensively to obtain adsorption equilibrium and rates (Czanderna and Thomas 1986). The great potential of the QCM is being exploited for both screening and evaluating advanced polymeric desiccant materials for this research.

To understand the molecular processes for water-solid adsorbent desiccant systems, there is an obvious opportunity to combine the use of QCM, infrared, and surface spectroscopies to correlate rates and amount sorbed with the chemical bonds formed (related to heats of adsorption) and surface composition (effects of chemical modification). Furthermore, any changes in the amount sorbed and the rate of desorption should result in changes in the bonding at the surface (infrared). Finally, experimental data in the literature are not sufficient for assessing the potential of polymeric materials as desiccants. The objectives of this research have been developed from the obvious unexplored opportunities for providing scientific understanding or information about candidate water desiccant materials and rationale for possible modifications of the adsorbents.

APPENDIX C

CRITERIA FOR IDENTIFYING POTENTIAL AND CANDIDATE ADVANCED DESICCANT MATERIALS

In 1985, about 300 articles were identified in a literature search for potential candidate ADMs. Because the sorption capacity of a desiccant is critical for its use in a DCS, the computerized literature search was carried out for articles containing the phrase water vapor and the word polymers. About half the literature citations were for articles in Japanese, Russian, or Eastern Bloc languages; these were not translated based on our best judgments from the English abstracts. In late FY 1987, the literature search was updated; about 70 additional publications concerning potential polymeric ADMs were identified. Nearly all these publications are in foreign languages, especially Japanese and Russian. Copies of the articles have been or are being secured, and translations will be obtained where appropriate.

C.1 Criteria Used for Ranking Potential Candidate Materials

There are two sets of parameters that could be applied for ranking the identified materials in a list of potential candidate ADMs. The first set is as follows: (1) cost, both initial and life cycle; (2) performance; (3) durability, lifetime, and how performance parameters depend on temperature; (4) availability; (5) processibility; (6) modifiability; (7) stability at temperatures below 100°C; and (8) specific heat. For polymeric materials, the most important initial criterion is 2. As a first approximation, polymers should have relatively uniformly good prospects for points 1, 4, 5, 6, and 7 and marginal values for 8. It was not expected that durability of polymers used as desiccants (3), would have been evaluated, and this expectation was correct (Czanderna and Thomas 1986).

C.2 ADM Performance Criteria

The second set of parameters considered were performance related and were divided into three categories: primary, secondary, and other criteria. These criteria were ranked and reviewed by several members of the SERI desiccant team before they analyzed the available literature references. The criteria, which are more detailed than previous listings, were generated by SERI researchers in 1985 (Czanderna and Thomas 1986). These now must be modified because of a computer parametric study (Collier, Cale, and Lavan 1986). The modified criteria in the following list are subjectively based on a combination of input obtained by the task leader from several sources, including verbal communications with K. Collier, GRI program managers, Kaiser personnel, Eaton personnel, J. Mitchell, D. Ruthven, and SERI task team members. The revised criteria are listed with brief explanatory statements.

Primary criteria for further narrowing the potential of polymeric materials as advanced desiccants are as follows:

1. Isotherm shape (Type I moderate as defined by Collier, Cale, Lavan [1986]): Silica gel has a linear-type isotherm, which results in an upper limit of 1.05 for the thermal COP.

2. Capacity change of at least 6% to 8% by weight between 5% and 60% R.H: Note that large capacities are not nearly as important as previously thought, which not only enlarges the list of polymeric potential ADMs but also of inorganic materials.
3. Rapid adsorption at 22°C: Rapid is interpreted to mean that most of the capacity change must be completed in less than 5 min to correspond to the anticipated exposure time in rotary commercial desiccant cooling systems (CDCSs).
4. Reversibility on desorption at 22°C for isotherm determination: Rapid desorption rates are helpful but not necessary because the desorption kinetics will be increased by elevated regeneration temperatures.
5. Reproducibility in 1 through 4 following regeneration as high as 80°C, i.e., the current anticipated regeneration temperature for a solar-based DCS. If higher regeneration temperatures are planned, then the 80°C must be increased accordingly.

Secondary criteria that will be applied to materials passing 1 through 5 include

6. Diffusivity of greater than 10^{-9} m^2/s: Qualitative aspects of diffusivity or permeation rates are automatically observed during studies with QCM and Sartorius microbalance techniques from 3 and 4.
7. Desorption rates of water at the regeneration temperature that provide sufficient capacity change in less than 5 min.
8. Heats of adsorption at or near 10.8 kcal/mol, which is the latent heat of vaporization of water: Higher heats of adsorption result in a decrease in overall DCS efficiencies.
9. Specific heats with $(dw/dx)/C_p$ greater than 0.5 gK/J for 5% to 80% R.H: This parameter is now thought to be less important than in 1985 and, in fact, does not have a wide range of variability for polymers.

Other criteria, which then need to be applied to materials that remain candidates after applying points 1 through 9, include cyclic stability, durability in pure water, synthetic air environments, and life-cycle costs that are competitive, with or without contamination by use in working environments.

Because the goal of our research is to measure the performance parameters of the material itself, the obvious engineering-related parameters (e.g., bed geometry, material form, desiccant size and shape, packing density, pressure drops, and heat and mass transfer) were not considered but could easily be factored into future concepts.

APPENDIX D

TECHNICAL APPROACH FOR STUDYING ADVANCED DESICCANT MATERIALS

The key technical questions were used to formulate our technical approach. The multiyear technical approach for studying the water vapor sorption by potential materials for use in regenerative DCSs consists of conducting experimental work and interpreting the data; thus, the necessary understanding of the reversible and irreversible processes that take place can be obtained. The following variables and processes are particularly relevant for experimental research on desiccant materials.

To accomplish the goals and objectives of this research, the technical approach for this project has been and will be to perform the following:

1. Identify, select, rank, and prepare for a study of potential ADMs.
2. Modify polymers or inorganic materials to improve their sorption performance, and synthesize new polymeric materials that are molecularly engineered to function as ideal ADMs.
3. Identify the performance criteria of ADMs, including sorption performance and durability.
4. Identify the necessary measurements for characterizing the water vapor sorption performance of potential ADMs.
5. Design, purchase, construct, install, and use the experimental apparatus necessary for characterizing the sorption performance and establishing the durability of ADMs.
6. Measure the sorption performance and determine relevant physical parameters of potential ADMs to establish which materials are candidate ADMs based on the criteria in point 3.
7. Determine the repeatability of the sorption performance of candidate ADMs from points 1, 2, 3, 4, and 6 as a function of sorption-desorption cycles at time intervals corresponding to DCSs and at regeneration temperatures planned for use in DCSs.
8. Determine the effect of chemical modification of ADMs and their surfaces on sorption performance.
9. Conduct fundamental scientific investigations to understand the interplay among composition, bonding, topography, surface area, pore volume, pore size distribution, morphology, and their changes during cycling and use in real environments.
10. Perform analytic and theoretical work, as needed, to assess the opportunities and limitations of candidate ADMs for use in the engineering configurations of contemporary DCSs.
11. Cooperate with others performing desiccant R&D to expedite the testing of candidate ADMs in engineering configurations.
12. Prepare reports, publications, and make presentations to disseminate the results of the work.

APPENDIX E

QUARTZ CRYSTAL MICROBALANCE APPARATUS

The commonly known QCM is actually a piezoelectric QC resonator mounted in an appropriate holder. Piezoelectric materials are used extensively as electromechanical transducers and highly stable oscillators for frequency control. For the latter application, mechanical and thermal stabilities are more important, and materials such as alpha quartz have been found to be valuable. Quartz has the smallest coefficient of the widely used crystalline solids, but the material can still be used in oscillator circuits to secure pg/cm^2 mass sensitivities. The effect of mass added to the frequency of a quartz oscillator has been used since the early days of radio, when frequency adjustment was accomplished by a pencil mark on the crystal.

It was established early that the cut, i.e., the orientation of the QC plate with respect to the crystallographic axes, had an important effect on the resonance frequency. For use as a piezoelectric crystal detector, only AT- or BT-cut quartz plates are useful. These crystals are two high-frequency plates that vibrate in a shear mode about an axis parallel to the major surface; these plates have low or zero temperature coefficients at the temperature of use and have surfaces that are antinodal in displacement. The temperature coefficients are a critical function of the angle of cut. The AT-cut is superior in temperature coefficient and mass sensitivity. The crystals used most frequently are 10- to 16-mm disks, squares, or rectangles that are approximately 0.19-mm thick. The metal electrodes are 300- to 1000-nm thick and 3- to 8-mm diameter and are made of gold, nickel, silver, or aluminum. The QC frequency depends on the physical dimensions of the quartz plate and the thickness of electrodes placed on it. The resonant frequency of a crystal is normally obtained using a frequency meter attached to the output of an oscillator circuit (Czanderna and Thomas 1986).

With an idealized model, a relationship was developed (Sauerbrey 1959) between the mass of metal films deposited on QCs and the change in frequency. The relationship, which was derived for QCs (AT-cut) vibrating in the thickness shear mode, is

$$\Delta f = -2.3 \times 10^{-6} f^2 \, \Delta m/A \ , \qquad \text{(E-1)}$$

where Δf is the change in frequency resulting from the coating (Hz), f is the frequency of the quartz plate (MHz), Δm is the mass of deposited coating (g), and A is the area coated (cm^2). The constant includes the density of quartz and the velocity of a wave in the shear mode. Equation E-1 predicts that a commercially available 6-MHz crystal, which has been chosen in this research, would have a mass sensitivity of about 12 ng/Hz for a coated area of 1 cm^2. The sensitivity factor for crystals used in our research is actually 14 ng/Hz.

If a desiccant material with an overall density of 1.4 g/cm^3 is placed on a QC, then a desiccant film 0.1 μm-thick with an area of 1 cm^2 would have a mass of 14 μg, so the limit of detectability of mass change would be 0.01%/Hz [100% × (14 ng/Hz)/14 μg], where ±0.1 Hz can be routinely monitored with our commercially available oscillator circuits. For thicker desiccant films, the percent mass sensitivity is even smaller. Because the interest is in desiccants with percent mass gains in water of more than 5%, the QCM sensitivity is more than sufficient, even if an active QC area of only 0.25 cm^2 is used. The mass measuring range of the QCM will permit studying polymer thicknesses that vary more than 100 times, so permeation rates can also be deduced.

For operation in a vacuum, the QC holder is an integral part of a vacuum system apparatus, as shown in Figure 2-2. The essential components of this holder include a 2.75-in. stainless steel Conflat® vacuum flange with feedthroughs for a thermocouple, cooling water, and the electrical leads needed to operate the oscillator. The essential components of the vacuum system include a source of pure water vapor, capacitance manometer, valves for manipulating gas pressures, pumps, and low-pressure gauges. Sample temperatures are measured with thermocouples. Detailed descriptions of the QCM and vacuum chamber components are available (Czanderna and Thomas 1986).

The advantages of the QCM for measuring the sorption of water vapor by ADMs are as follows:

- The fundamental water sorption properties of desiccant materials can be studied in the absence of any engineering design restrictions.
- An appropriate mass sensitivity (14 ng/Hz cm^2) is obtained using commercially available equipment. For example, a 100-nm-thick polymer film with a mass of 14 ng on a 1-cm^2 QCM results in detectable mass changes of 0.01%, or 10% of a single monolayer of an adsorbed gas is detectable for contaminant studies (a precision of ±0.1 Hz is obtained with our QCM).
- The response time is fast, i.e., 2 s per point.
- It can be used in pure water vapor at pressures comparable to the relative humidity in actual desiccant systems. Thus, the sorption kinetics of the desiccant can be studied in the absence of any gas-side diffusion effects.
- It is simple to use and is not sensitive to shock or vibration.
- An accuracy of < ±2% can be achieved.
- It can easily be adapted for simultaneous use with infrared or surface analysis equipment.

Some of the principal limitations of the QCM are as follows:

- Samples must be coated onto the QC and must adhere to it, which presents a particular challenge when studying particulate materials.
- Only one temperature (or a narrow temperature range) can be studied with a given crystal at the maximum sensitivity.
- Liquid samples are not easily studied.
- Condensation of unknown gases on the sample or volatile materials in the sample may cause problems in securing the actual water sorption.

APPENDIX F

ISOTHERM DETERMINATION AND KINETIC AND CYCLIC STABILITY STUDIES

F.1 Procedures Used for Determining Isotherms

After mounting the polymers of interest onto QCs and obtaining the mass of the attached polymer, the crystal is then attached to the oscillator head and bolted onto the vacuum system. The sample chamber is pumped to the 10^{-8} torr range with the sample at about 22°C, and the oscillator mass is zeroed after the mass loss or gain has equilibrated. The system temperature is equilibrated to 22.1°C, and water is admitted to the samples to a pressure of 1 torr. The system is allowed to equilibrate (both pressure and mass measurements). The water vapor pressure is then increased in about 2-torr increments, and the pressure and mass measurements are taken during the approach to equilibrium and after equilibrium is reached. After reaching the desired maximum pressure (16 torr in this work), the process is reversed by decreasing the water vapor pressure in about 22-torr decrements followed by equilibration intervals. (There is no design restriction for making pressure changes of about 2 torr, which were chosen for our convenience; any desired pressure change can be chosen to as high as 20 torr at 22.1°C. Higher pressures can be studied by increasing the ambient temperatures of the entire QCM and vacuum apparatus.)

In general, data for the first isotherm determination were obtained at about 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, and 80% R.H. by increasing the water vapor pressure from a vacuum of less than 10^{-7} torr to an initial pressure of about 1 torr (5% R.H.) and monitoring the uptake for about 45 min. The capacity changes reported in the isotherms for all polymers are relative to the sample mass after evacuation at 22.1°C. The percent of water uptake is calculated by multiplying the area of polymer times the mass of water gained (or lost) times 100% and dividing by the mass of the polymer on the crystal. The percent water vapor uptake is given by

$$\%\ H_2O = \frac{0.0785\ d^2\ (\Delta m)}{M}\ , \qquad \text{(F-1)}$$

where d is the diameter in centimeters of the polymer coating on the QC, Δm is the change in ng/cm^2 of the QCM readings between vacuum and at any water vapor pressure, and M is the sample mass in µg. M was corrected for the loss during outgassing by using $M = M_o - \pi d^2 \Delta m_o/4$, where M_o is the sample mass measured in air, and Δm_o is the ng/cm^2 loss during outgassing. The factor 0.0785 d^2 results from the polymer coating covering a larger area than the sensing area (0.58 cm^2) of the QC that yields the mass reading in ng/cm^{22}. This factor then corrects the polymer mass (M) to the fraction of M that is coating the sensing area of the QC. The maximum value for d is 1.4 cm, the diameter of the crystals used in this work. The actual value for d, which is obtained by combined visual and optical inspection of the polymer coating, has typically ranged between 1.2 and 1.3 cm.

The R.H. percent is calculated by multiplying the Baratron pressure reading times 100% and dividing by the saturation pressure of water at the system temperature. These calculations have been simplified by carrying out our sorption studies at 22.1°C, where the saturation vapor pressure of water is taken as 20.0 torr. The actual vapor pressure at 22.1°C is 19.95 torr. Thus, each 1 torr corresponds to 5% in R.H., where R.H. is the most widely used representation of the partial pressure of water in desiccant cooling R&D and applications.

Isotherm shapes obtained by the QCM compare favorably with those measured by other methods. Examples of isotherms obtained with the QCM are given in prior reports (Czanderna and Thomas 1987a) and in Section 4 of this report. The water uptake is accurate within the limits described.

F.2 Kinetics of Sorption and Desorption by Polymers That are Candidate ADMs

After each pressure increase or decrease that is made while obtaining the isotherm data, the approach to the equilibrium mass gain or loss was recorded at 2-min intervals through the first 20 min and then at 10-, 20-, or 30-min intervals for 4 to 6 h. In the semiautomatic operational mode of the QCM, these data are printed but are not plotted for visual display or interfaced to a graphics terminal. Thus, all sorption-desorption kinetic curves must be plotted manually or evaluated by inspecting the printout of the data. The latter method was chosen, and qualitative statements of fast, intermediate, and slow are assigned after visual inspection of the data. The definitions are as follows: fast, more than 90% of the incremental or decremental mass change occurred in the first 10 min; intermediate, more than 90% of the mass incremental or decremental change occurred in the first 60 min; and slow, less than 90% of the incremental or decremental mass change occurred during the first 60 min. For CDCSs, only fast kinetics will qualify a material as a candidate ADM. Intermediate kinetics do not necessarily disqualify a material as a candidate, and slow kinetics probably disqualify a material.

Czanderna 1988, Tables 4-1 and 5-1 illustrate the type of data that can be retrieved for the materials. Plots of the sorption and desorption kinetics are shown in Figures 5-22 and 5-23 of this report for several different polymers after increasing the water vapor pressure from 5%, 30%, or 60% R.H. or decreasing it from 60% or 80% R.H. These curves show that the kinetics are fast at all pressures. Similar data are archived in several thousand pages of printer output secured while measuring the isotherms. The data for the candidate polymeric materials listed in Section 1.4 of this report are especially important for planning future experiments and for potential technological use of these polymers as ADMs.

F.3 Cyclic Stability Studies

As discussed in Appendix C, a candidate ADM must exhibit reproducible sorption behavior after being subjected to several tens of thousands of adsorption and desorption cycles. From our study of the literature, major changes in the sorption behavior of many polymers occur in the first one or two cycles. Repeated measurements of sorption isotherms have not been undertaken in previous work or in this research. We have subjected several polymers to 3 to 9 sorption cycles by simply remeasuring the isotherms. Typical results for the cyclic adsorption and desorption of water vapor are shown in Czanderna (1988) for SPSS, PAAAS, and CSSS for the first three cycles in Figures 5-24 through 5-29. The cyclic reproducibility is excellent for the first three cycles. In contrast, similar adsorption data obtained for four cycles of polyethylene oxide show a dramatic change in adsorption behavior from the first to the second cycle and continuing changes for the next two cycles.

The changes quite likely result from physical processes occurring within the polymer because of the adsorption and desorption cycles.

APPENDIX G

SARTORIUS MICROBALANCE

The need for placing an existing Sartorius microbalance system into operation was established in early 1987. During 1988, it was attached to the gas-handling and pumping station of the present QCM apparatus, as shown below. The Sartorius microbalance retains all the essential advantages of the QCM cited in Appendix E and eliminates all the limitations cited. The principal limitation of the Sartorius microbalance or any other beam microbalance is that only one sample can be studied at a time. The capacity of the balance is 5 g, with a sensibility of less than 1 µg; samples of any configuration can be suspended in an appropriate container (e.g., a hemispheric gold cup); and accuracy to better than 0.01% can easily be assured. As of December 1989, the Sartorius microbalance system was ready to be tested for operability.

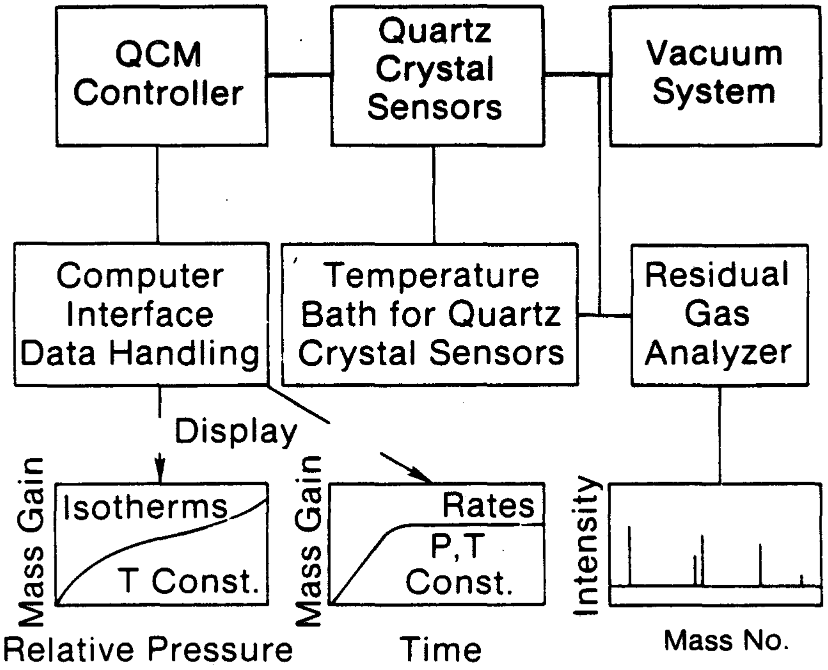

Figure G-1. **Block diagram of arrangement of a combined QCM and Sartorius microbalance apparatus**

APPENDIX H

STATEMENT OF WORK

SYNTHESIS/MODIFICATION OF DESICCANT POLYMERS

I. OBJECTIVE

The technological objective of this work is to synthesize or to modify desiccant polymers as next-generation, low-cost materials with which solar radiation or heat from another low-cost energy source can be used for regenerating the water vapor sorption activity of the desiccant. The scientific objective of this task is to determine how the desired sorption performance of advanced desiccant materials can be predicted by understanding the role of materials modifications and their surface phenomena, and their interaction with water vapor.

The purpose of advanced desiccant materials (ADM) research and development (R&D) is to provide new materials options for desiccant cooling systems (DCS) by identifying materials with optimal performance in the temperature range used in a DCS in which the sorption activity of the desiccant can be routinely regenerated with an appropriate energy source. The life-cycle cost (i.e., initial cost, performance, and durability) has a direct relationship on the cost-effective deployment of any regenerative DCS. Identification of low-cost materials with extended lifetimes and desirable sorption properties for use in DCS can be anticipated from a sustained R&D effort. Thus, an ADM can advance solar buildings technology not only by lowering the cost of commercial solid desiccant cooling systems (CDCS) to compete with conventional air-conditioning, but also by eliminating the need for adding peak-load generating capacity by electric utilities.

II. BACKGROUND

In the early work with solid desiccants for DCS applications, silica gel was used as the desiccant because of many desirable properties and the available information about it. The possible need for an "ideal desiccant" was conceived by Czanderna in 1983 and the optimum sorption properties of a desiccant material in DCS were identified in a systems analysis study in 1985 (Collier). If an ideal desiccant can be identified, the coefficient of performance of a DCS can be improved from 0.85 to 1.05, which can now be obtained with silica gel, up to 1.3 to 1.4 or close to the theoretical maximum. At the same time, the cfm/ton can be reduced from a range of 310 to 400 for silica gel to a range of 200 to 250 for an ideal desiccant. If both of these factors are achieved, DCS could be cost-competitive with other current air-conditioning systems, and this is not possible for silica gel (Collier).

Prior to Colliers' conclusions in 1985, this project was initiated to identify new, low-cost, next-generation materials with the desired water vapor sorption performance, i.e., isotherm shape, sorption capacity, heat of adsorption, adsorption and desorption kinetics, and cyclic stability. Of the commercially available inorganic (e.g., alumina gel, chromia gel, charcoal) and organic materials, over 25 commercially available polymeric materials were selected as potential candidates for use in desiccant cooling systems (DCS). By considering the available polymeric desiccants, scientists note or have demonstrated that polymers have many potential advantages, e.g., high sorption capacity, high diffusivity, low regeneration temperatures, cyclic and long-term stability, modifiability, fabricateability, and low cost. Polymers have outstanding potential for the "molecular engineering" of an ideal desiccant. Polymeric materials could not only serve as both the desiccant and support structure in a desiccant wheel, but also could be replaced easily and inexpensively if their water sorption capacity degrades for any reason. Accordingly, the initial emphasis of this research was to characterize the water sorption performance of polymeric materials that could be used in an economically competitive DCS. Of over 23 commercially available polymers studied in FY86 and FY87, nine were identified as being serious candidates for DCS applications. One of these, polystyrene sulfonic acid sodium salt (PSSASS), is being studied by Cargocaire Engineering as a potential replacement for their current desiccant, and their initial results show some promise. Since PSSASS is not an "ideal" desiccant, the focus of the project for FY88 was directed towards modifying two commercially available polymers and synthesizing a new promising non-cross-linked polymer.

The multiyear technical approach for accomplishing the purpose and objectives of the ADM effort consists of conducting experimental work and interpreting the data to obtain the necessary understanding of the phenomena involved. Part of the approach followed is (will be) to:

(1) Identify, select, prioritize, and prepare for study potential ADM; and

(2) Modify polymers and/or inorganic materials to improve their sorption performance and synthesize new polymeric materials that are "molecularly engineered" to function as an "ideal" ADM.

III. RECENT PROGRESS

During FY 1988, publications 1 and 2 were completed and give detail on all prior work on this task. Polystyrene sulfonic acid sodium salt (PSSASS) and sodium polystyrene sulfonate (SPSS), which are both commercially available, have been used for our polymer modification studies. The SPSS studied to date has a narrower molelcular weight (MW) distribution than the PSSASS. From sorption capacity measurements of PSSASS and SPSS with different MW, it was demonstrated that the isotherm shape depends on the MW. The best isotherm shapes are obtained for MW between 5,000 and 60,000, but the optimum MW has not been deduced. Outside this MW region, the isotherms become more linear and less type 1 moderate below 60% relative humidity (R.H.) (Figure 1). Accordingly, the first modification has been to prepare polystyrene (PS) with a MW of 6,000 and 50,000. These MW are not available commercially. The second modification has been to sulfonate the PS to the acid form, i.e., PSSA, and exchange the acid form with sodium ions to form PSSASS. The PSSAs have been prepared with targeted sulfonic acid percentages of 20, 40, 60, and 80%, which have then been exchanged to form the corresponding PSSASS. The preliminary sorption data on these PSSASS indicate the best isotherms are obtained between 40 and 80% sulfonation, so again there is sensitivity to the polymer synthesis method. Other modifications planned include exchanging PSSA either with lithium ions or cesium ions. This third modification may have the most dramatic influence on the isotherm shape.

IV. PUBLICATIONS

1. "Polymers as Advanced Materials for Desiccant Applications", A. W. Czanderna, SERI/PR-255-3308, August, 1988.
2. "Advanced Desiccant Materials Research: 1988", A. W. Czanderna and H. H. Neidlinger, SERI/PR-255-3443, December, 1988 (DRAFT).

V. SCOPE AND TASKS

As evidenced by the preceding sections, the Solar Energy Research Institute (SERI) has an interest in polymers that can serve as advanced materials, for use in desiccant cooling systems (DCS). Please see SERI/PR-255-3308, especially sections 1.1-1.4, 1.6, 2.0, 4.0, 6.0, and appendices A, D, and F. SERI needs to have polymers modified, specifically, polystyrene sulfonic acid (PSSA) and its salts, and new formulations synthesized that will provide the desired water vapor adsorption properties (ca 22°C and from 5 to 80% r.h.) and desorption properties as outlined in Section 2.0, and as shown in Figure 1 for Type 1, moderate, behavior. In the remainder of calendar 1989, it needs to have one "new" hydrophilic desiccant polymer synthesized, and modifications made in the counterions exchanged with PSSA.

To accomplish the polymer preparation needs in calendar 1989, the subcontractor will complete tasks 1 through 3. The formulations prepared in tasks 1 through 3 are to be soluble in water or water-based solvents, stable to at least 90°C in moist air, and have the potential for being attached to a polymeric support structure. The polymer should be soluble in a solvent that could permit it to be impregnated into a structural matrix (1 mm diam. channels), not swell excessively at its water sorption capacity of 20-30% by weight or more, be stable for cyclic (>1000,000 times) regeneration (desorption) at 80-100°C, and have potential for a mass-produced cost below $20/lb.

Task 1

Synthesize formulations of an appropriate polymer (e.g., AMPS, acrylomido methyl propyl sulfonic acid) that may meet the performance criteria for use in DCS. If the results of SERI's initial sorption performance characterization of these formulations are promising, then modifications of it will be carried out with an objective of further improving the isotherm data.

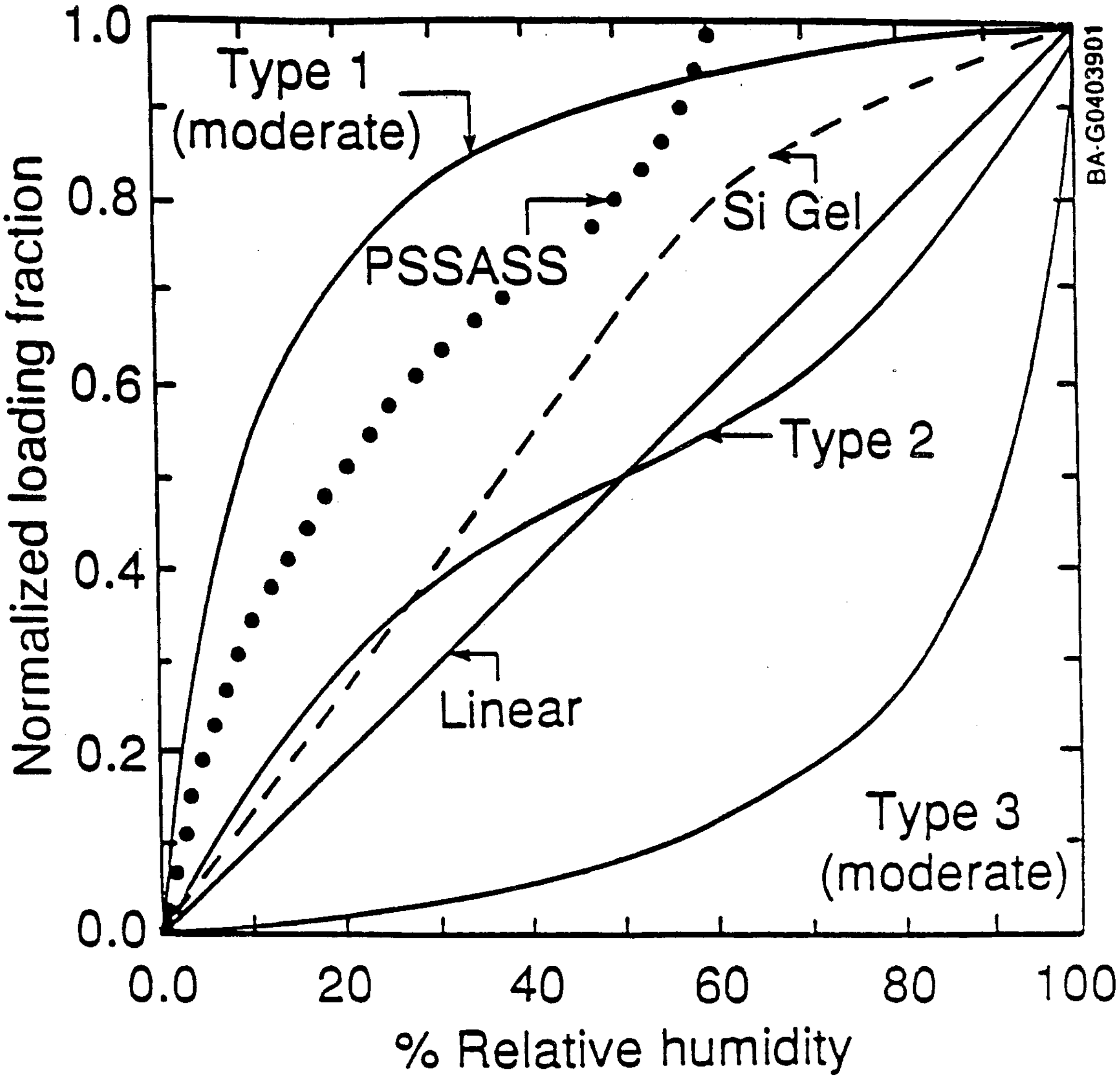

Figure 1. Isotherms showing the relative capacity for water sorption for silica gel, PSSASS, and the comparisons with Colliers' Type 1 Moderate, Type 2, Linear, and Type 3 Moderate.

Task 2

(a) Prepare polystyrene sulfonic acid (PSSA) with a specific MW in the range of 6,000 to 30,000; and at a specific sulfonation between 55 and 80%.

(b) Determine the specific MW and % sulfonation.

Task 3

Prepare salts of the PSSA made in Task 2 with Li^+, Na^+, K^+, and Cs^+.

VI. TECHNICAL MILESTONES AND DELIVERABLES

The milestones listed below shall be used to monitor progress. They are listed in the number of weeks after the subcontract work is begun and are spread over a performance period of five months.

Weeks	Milestone No. and Description
2	1. Reach agreement on the polymeric formulation to be used in Task 1 and on the targeted MW and % sulfonation in Task 2.
12	2. Deliver to SERI (via an appropriate transmittal) for its water vapor characterization quantities of at least 500 to 1000 mg of the polymers made in Task 1. The concentration of the solution may range from 1g/5 ml to 1g/500 ml, where the more dilute solutions simplify SERI's work.
14	3. Deliver to SERI as per Milestone 2 for the PSSA made in Task 2 within one week after its preparation.
18	4. Deliver to SERI as per Milestone 2 for the salts of PSSA made in Task 3 within two weeks after their preparation.
22	5. Provide SERI with the written details of the preparation procedures for those materials made in tasks 1 through 3 that SERI determines to be of interest as ADM.

VII. REPORTING

A monthly progress letter shall be mailed during the last week of the month to the SERI technical monitor. The purposes of this letter are primarily to report (1) if planned internal progress is proceeding to meet the timetable for providing the deliverables in Section VI, (2) to confirm any shipments of deliverables, and (3) to provide a general (and brief) overview of the procedures being used. This letter should not be longer than one, single-spaced, typewritten page, since the procedural details that might be required will be delivered under number 5 in Section VI.

VA-89-21-2

Polymers as Advanced Materials for Desiccant Applications: 1—Commercially Available Polymers

A.W. Czanderna, Ph.D.

ABSTRACT

This paper is concerned with identifying solid polymeric materials that might be used in desiccant cooling systems (DCS) that process water vapor in an atmosphere to produce cooling. Background information is presented that includes an introduction to DCS and the role of the desiccant as a system component. The experimental method for measuring water vapor sorption by desiccants is described for a quartz crystal microbalance (QCM). The water vapor sorption performance criteria are identified for narrowing the potential advanced desiccant materials (ADM) to a few candidate ADM. Measurements are presented for the sorption performance of 23 commercially available polymeric potential ADM materials with the QCM. The data include sorption isotherms, the rate of adsorption and desorption at each pressure increment or decrement, and cyclic stability. By applying the required performance criteria, the candidate polymers are: polystyrenesulfonic acid sodium salt, sodium polystyrene sulfonate, polyacrylamide-carboxyl modified, polyacrylic acid ammonium salt, poly(methacrylic acid) sodium salt, poly(n-vinylacetamide, vinyl sulfonate) sodium salt, polyacrylic acid sodium salt, cellulose sulfate sodium salt, and methyl cellulose.

INTRODUCTION

Desiccant Cooling Systems

This paper is concerned with solid materials used as desiccants for desiccant cooling systems (DCS) that process water vapor in an atmosphere to produce net cooling. Since mass transfer occurs between the system and its environment, these systems are commonly referred to as "open-cycle" systems (Collier et al. 1982). All these systems use a liquid or solid material called a desiccant to remove water vapor from the air either by adsorption onto or into a solid desiccant or by absorption into the liquid desiccants. This paper will focus on the solid-type desiccant system, although the reader will recognize the opportunity using liquid-based systems.

Systems with solid desiccants are currently used in industrial air-drying applications and in DCS. These use a desiccant-laden wheel in which air may flow in the axial direction only. The solid desiccant (typically silica gel and/or lithium chloride) is mounted onto a wheel and the air to be dried flows through one side of the wheel while the desiccant on the other side of the wheel is being dried by an externally heated airstream. These two airstreams are kept physically separated to maintain the distinctly separate functions of air dehumidification and desiccant regeneration. The historical development that led to present commercial systems has been summarized by Collier et al. (1982).

The commercial systems are primarily intended for specialized applications that require dehumidifying air and usually do not produce a significant net cooling. There are important differences in design philosophy between solar-regenerated desiccant cooling systems and commercial desiccant dehumidifiers. The most important difference involves the thermal and electrical coefficients of performance (COP). For many years, commercial desiccant dehumidifier manufacturers have chosen markets in which vapor-compression equipment cannot compete, i.e., applications where extremely dry air is required or where latent cooling loads are high. The energy requirements to achieve these conditions have not been a major concern and, as a consequence, the desiccant dehumidifiers often have very low thermal and electrical COP.

Commercial solar-regenerated desiccant cooling machines must compete with vapor compression as well as all other space-cooling technologies, so both electrical and thermal COP are of primary concern. From thermodynamic analyses of desiccant cooling cycles, it is apparent that the adsorption characteristics of the desiccant can have a large influence on the cooling capacity and COP of the cycle (Collier et al. 1982; Jurinak 1982). This effect was quantified in a recent computer parametric systems analysis study (Collier 1986). Collier concluded that if an ideal desiccant can be identified, the thermal COP of a DCS can be improved from 0.85 to 1.05, which can now be obtained with silica gel, up to a minimum of 1.3 to 1.4 or close to the theoretical maximum. At the same time, the cubic feet per minute per ton (cfm/ton) can be reduced from a range of 310 to 400 for silica gel to a

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range of 200 to 250 for an "ideal" desiccant. The reduction in cfm/ton must not be overlooked since this factor can reduce the physical size of commercial DCS while keeping electrical parasitic consumption low. If both of these factors were achieved, DCS could be more cost competitive with other current air-conditioning systems; this is not possible for silica gel (Collier 1986).

Silica gel and lithium chloride are now the most widely used desiccant materials used in wheel geometries in DCS. Extensive optimization studies of the engineering design of DCS units have been carried out using silica gel (e.g., Barlow 1982; Jurinak 1982; Pesaran and Mills 1984; Schlepp and Barlow 1984; Schlepp and Schultz 1984; Pesaran et al. 1986). Models in systems analysis studies for estimating the achievable thermal and electrical COP also use the properties of silica gel since they have been documented extensively over several decades (Parent 1985). Since the water sorption properties of the desiccant *are crucial to the performance* of any system, this desiccant materials research effort was initiated to search for and measure the properties of materials that could not only become better desiccants than silica gel but also approach the ideal desiccant material in its sorption performance. In addition, manufacturing methods with new materials could have a profound impact on reducing the dehumidifier cost.

Purpose of Advanced Desiccant Materials Research

One purpose for performing long-range research on materials is to secure an understanding of the behavior of low-cost, high-performance technological materials, with a goal of extending the lifetime of these materials, or to identify new materials that will offer new options for components used in operating systems. The cost-effective deployment of DCS is currently limited by the sorption performance, durability, and life-cycle cost of the *inorganic* materials used. Long-term materials research is needed that focuses on improving the properties of advanced desiccant materials (ADM) and on identifying the reasons for degradation of their sorption performance.

Polymers as Advanced Desiccant Materials

The relationship of desiccant materials to DCS and background information about studies of ADM have been summarized (Czanderna and Thomas 1987). Polymers must satisfy the same general criteria as any desiccant material. They must have a favorable performance/cost ratio, provide satisfactory performance, and have cost-effective lifetimes; widely available materials need to be certified, modified, or, in some cases, developed specifically for use in DCS. Some of the important parameters for the water solid-desiccant-material system include isotherm shape, sorption capacity, heat of sorption, rate of sorption at or near the desiccant bed temperature of 68°F to 131°F (20°C to 55°C), rate of desorption at an elevated temperature, physical and chemical stability of the desiccant, and cyclic repeatability of the sorption amount and rates. Some important conclusions and recommendations on these parameters were reached in the recent modeling study for regeneration at 320°F (160°C) (Collier 1986), but the possibility of identifying new materials with optimal properties was not considered.

From our literature search (Czanderna and Thomas 1986), we identified both inorganic and organic (i.e., polymeric) materials as potential candidate ADM for use in DCS. To focus our research, we initially selected 21 commercially available *polymeric* materials for further study. These have been listed in previous reports (Czanderna and Thomas 1986; Czanderna 1988). The process used to narrow the list of more than 300 commercially available polymers to those summarized has also been reported (Czanderna and Thomas 1986). We identified several additional polymers as our studies progressed.

By considering the available polymeric desiccants, we note the following:

- Polymers have the potential of being modified so that sorption isotherms of both the desired shape and heats of adsorption of about 2508 kJ/kg are obtained.
- Polymers have the potential for sorbing water from 5% to more than 80% of their own weight.
- Polymers have the potential for being readily fabricated into shapes required for DCS, e.g., a honeycomb structure 10 *x* 0.04 *x* 0.06 in (25 *x* 1 *x* 1.5 mm).
- Polymer structures have the potential for being synthesized to provide high diffusivities of water vapor through the material.
- Polymers have the potential for being regenerated at temperatures below 176°F (80°C) for thermally desorbing water.
- Polymers have the potential for maintaining long-term stability through thousands of sorption-desorption cycles.
- Commercial polymers are available at less than $2.00/lb, comparable to the cost of commercial-grade silica gel.

Accordingly, polymeric materials could not only serve as both the desiccant and the support structure in a desiccant wheel but also could be replaced easily and inexpensively if their water sorption capacity degrades. The initial need of this research was to characterize the water sorption performance of commercially available polymeric materials that could serve in an economically competitive DCS.

Three key technical questions in seeking candidate polymers for DCS are the following: (1) Will any commercially available polymer have the properties required for use in a DCS? (2) Can the candidate commercially available polymeric material be modified to improve performance properties such as isotherm shape, heat of adsorption, regeneration temperature, cyclic stability, and diffusivity? (3) If commercially available polymers are not suitable, can laboratory-prepared polymers be synthesized with suitable sorption, desorption, and stability properties?

Our technical approach was chosen to be able to address the above questions as well as other questions such as the influence of sample size, impurities, and other degradation processes if the initial questions are successfully answered. The apparatus used for screening the potential candidate polymers, the polymers used, and the results of our initial studies will now be presented.

EXPERIMENTAL MEASUREMENT OF WATER VAPOR SORPTION BY POLYMERS

The experimental apparatus for measuring the water vapor sorption by a solid is conceptually simple. An arrangement is needed where a solid can be surrounded by pure water vapor (or a partial pressure of water in the ambient atmosphere) and the number of water molecules that bond to the solid can be measured. A vacuum system can be used to control the gas (vapor) pressure over the solid. There are three basic methods for directly measuring the rate of gas adsorption and the equilibrium amount of vapor adsorbed by a solid: (1) gravimetric, (2) volumetric, and (3) radiotracer. The last is excluded since it would require tritiated water and offers no obvious advantages over gravimetric techniques. Gravimetric techniques have many advantages over volumetric techniques (Czanderna and Vasofsky 1982; Gregg and Sing 1982; Czanderna and Wolsky 1980), especially for water vapor sorption studies. Water is one of the most difficult vapors to work with for analysis when using vacuum systems, but the determination of adsorption isotherms and the rate of adsorption and desorption of water can be carried out routinely with gravimetric techniques.

Quartz Crystal Microbalance Apparatus

Of the available gravimetric techniques, the beam microbalance and the quartz crystal microbalance (QCM) are the two best choices when the advantages and limitations of all microbalances are considered (Czanderna and Wolsky 1980). We chose to use a QCM for our initial studies because of the commercial availability of QCMs and their ease of use for studying the sorption of water by materials at or near 68°F (20°C) (Lu and Czanderna 1984). The experimental system, which is shown schematically in Figure 1, consists of a vacuum system, a residual gas analyzer, a QCM system with five quartz crystal (QC) sensors, and a temperature bath for the QCM. These components and their operation have been described previously (Czanderna and Thomas 1986; Czanderna and Thomas 1987b).

The commonly known QCM is actually a piezoelectric QC resonator mounted in an appropriate holder. Piezoelectric materials are used extensively as electromechanical transducers and as highly stable oscillators for frequency control. The resonant frequency of a crystal is normally obtained using a frequency meter attached to the output of an oscillator circuit. Using an idealized model, a relationship was developed (Sauerbrey 1959) between the mass of metal films deposited on QCs and the change in frequency. The relationship, which was derived for QCs (AT-cut) vibrating in the thickness shear mode, is $\Delta f = -2.3 \times 10^{-5} f^2 \Delta m/A$, where Δf is the change in frequency due to the coating (Hz), f is the frequency of the quartz plate (MHz), Δm is the mass of deposited coating (Kg), and A is the area coated (m^2). The constant includes the density of quartz and the velocity of a wave in the shear mode. The relationship predicts that a commercially available 6 MHz crystal, which has been chosen in this research, would have a mass sensitivity of *about* 12 ng/Hz for a coated area of 10^{-4} m^2. The sensitivity factor for crystals used in our research is actually 0.14 $mg/m^2 \cdot Hz$.

If a desiccant material with an overall density of 1400 kg/m^3 is placed on a QC, then a desiccant film 3.94 nin (0.1 μm) thick with an area of 10^{-4} m^2 would have a mass of 14 μg, so the limit of detectability of mass change would be 0.01%/Hz [100% x (14 ng/Hz)/14 μg], where ±0.1 Hz can be routinely monitored with our commercially available oscillator circuits. For thicker desiccant films, the percent mass sensitivity is even smaller. Since the interest is for desiccants with percent mass gains in water of more than 5%, the QCM sensitivity is more than sufficient, even if an active QC area of only 25 mm^2 is used. The mass measuring range of the QCM will permit studying polymer thicknesses that vary by more than 100 times, so permeation rates can also be deduced.

For operation in a vacuum, the QC holder is an integral part of a vacuum system apparatus (Czanderna and Thomas 1987b). The essential components of this holder include a 2.75 in (69.85 mm) stainless steel vacuum flange with feedthroughs for a thermocouple, cooling water, and the electrical leads needed for operating the oscillator. The essential components of the vacuum system include a source of pure water vapor, capacitance manometer, valves for manipulating gas pressures, pumps, and low-pressure gauges. Sample temperatures are measured with ther-

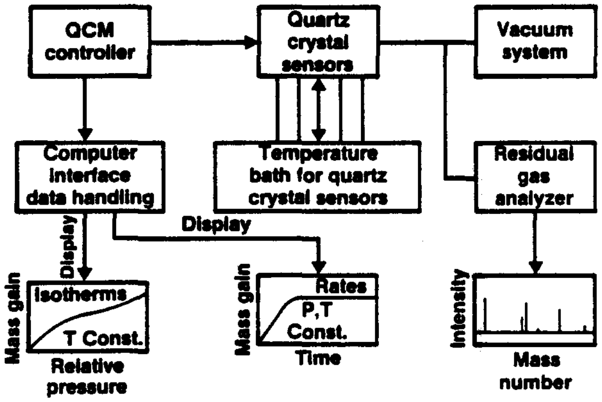

Figure 1 *Block diagram showing the principal components of a quartz crystal microbalance apparatus*

mocouples. Detailed descriptions of the QCM and vacuum chamber components are available (Czanderna and Thomas 1986).

The advantages of the QCM for measuring the sorption of water vapor by ADM desiccant materials are as follows: (1) the fundamental water sorption properties of desiccant materials can be studied in the absence of any engineering design restrictions; (2) an appropriate mass sensitivity is obtained using commercially available equipment; (3) the response time is fast, i.e., two seconds per point; (4) it can be used in pure water vapor at pressures comparable to the relative humidity in actual desiccant systems, which means the sorption kinetics of the desiccant can be studied in the absence of any gas-side diffusion effects; (5) it is simple to use and is not sensitive to shock or vibration; (6) an accuracy of < 2% can be achieved; and (7) it can be easily adapted for simultaneous use with infrared or surface analysis equipment.

Some of the principal limitations of the QCM are the following: (1) samples must be coated onto the QC and must adhere to it, which presents a particular challenge when studying particulate materials; (2) only one temperature (or a narrow temperature range) can be studied with a given crystal at the maximum sensitivity; (3) liquid samples are not easily studied; and (4) condensation of unknown gases on the sample or volatile materials in the sample may cause problems in securing the actual water sorption.

Polymer Selection

A ranked listing of potential polymeric advanced desiccant materials has been published based on the relatively sparse information available in the open literature (Czanderna and Thomas 1986). The only primary information that we were able to use was the sorption capacity and, in many cases, the isotherm shape. There were no permeation or diffusivity data given when isotherm data were given. When given, the permeation coefficients available were typically in the 10^{-10} to 10^{-12} m^2/s range, or slower than desired for DCS. The permeation rates in polymers depend strongly on the properties, but no evidence was found for any systematic synthesis effort to improve the diffusivities of water in polymers. In fact, synthesis efforts have been concentrated on retarding diffusivities for the obvious applications in corrosion protection. Finally, no important data published about the kinetics of water adsorption or desorption were found nor were any studies of the cyclic reproducibility for either the capacity or sorption rate reported. The only type of comments found were "adsorption is fast" or the isotherms were reproducible after "several cycles of measurement." Some polymers swell during water vapor adsorption, and this could be detrimental to the pressure drop of air in a working system.

The polymers studied to date, the acronym used in the remainder of this paper, and the commercial source are listed in Table 1. The solvent evaporation procedure was used to mount all the polymers listed in Table 1 on a QC.

Preparation of Polymers for QCM Studies

The following standard procedure generally has been followed for mounting the polymers onto QCs for subsequent study in the QCM apparatus. The QCs are Part No. 008-010, "crystals," and were obtained in boxes from a New York company. The crystals were not reused under any circumstances. Before mounting a polymer, we cleaned these crystals by removing a new crystal from the LH box, rinsing three times with methanol, rinsing three times with ethanol, and drying between halves of lint-free absorbent towels. The crystals are handled with tweezers cleaned in the same way. After cleaning, a crystal is weighed three times to the nearest 5 to 10 µg. The polymer mass is determined by weighing the crystal in air again after applying the polymer by a solvent casting process. The sample mass determination currently limits the *accuracy* of all our sorption data to between 4% and 20%. The accuracy can be improved to better than 2% by using a better microbalance than the one currently available. For an initial screening, we strive to apply 100 to 500 µg of polymer from a solution of the polymer.

The standard procedure we have adopted for dissolving a polymer (before mounting) is to weigh out 0.1 g of polymer, add it to 15 ml of 200-proof ethanol in a disposable specimen cup and rinse the boat with 10 ml of ethanol, and stir the polymer/solvent mixture with a magnetic stirrer until the polymer dissolves. After three hours, if the polymer does not dissolve, water is added in 5 ml increments where the first increment = 15% H_2O/85% ethanol; the second increment = 30% H_2O/70% ethanol; the third increment = 37.5% H_2O/62.5% ethanol; and the fourth increment = 45% H_2O/55% ethanol. Descriptions of detailed procedures for preparing several different polymers are given (Czanderna 1988) as examples of the effort required to secure satisfactory solutions of polymers. For cases where some of the polymer dissolves and some remains in solution, the undissolved component may be cross-linked and is filtered or the solution decanted as needed. This was necessary for several of the polymers tested so far.

The procedure for obtaining a uniform deposition of polymers onto the QC is basically a solvent evaporation process. Only two drops of polymer solution are initially deposited onto the center of the crystal before the initial weighing. The polymer is deposited onto the gold-covered crystal and care is taken to prevent any material from depositing onto the side of the crystal with the electrode configuration. Uniform coverage is essential so the polymer solution is added drop-by-drop onto the center of the QC. Our experience is that uniform coverage is obtained when the polymer solution wets the crystal. The solution concentration is chosen so that 50 to 100 µg of polymer will be obtained from each drop. Additional drops are added as needed for the targeted mass range.

After determining the mass of polymer mounted on a QC (in room air), we mount the QC on an auxiliary oscillator head to establish that the polymer-coated QC operates when a high-frequency oscillator is used to drive the crystal. Many times, a mounted polymer will result in a "fail" indication by the QC display of the QC power supply. When this occurs, another sample is prepared as described above. (Since the "fail" has only been a minor annoyance to progress on the project, we have not made an effort to establish what causes the "fail" indication but presume it is because the adhesion is insufficient between the QC surface and the polymer coating.) After obtaining a mass reading by the QCM power supply, the polymer coating is inspected visually and microscopically for lateral uniformity. The adverse influence of nonuniform coatings on the accuracy has been discussed (Czanderna 1988).

For improved accuracy of the isotherm capacity data, the polymer mass determined in laboratory air needs to be corrected for the loss in mass during outgassing. This correction in mass may be as much as 15% to 20% of the sample mass for the most hygroscopic polymers and will be made in future work. However, for purposes of the initial screening, the additional procedures required were not implemented to expedite completion of the initial work. By using uncorrected sample masses, we understate the actual percent weight gains.

Procedures Used for Determining Isotherms

After mounting the polymers of interest onto QCs and obtaining the mass of the attached polymer, the crystal is then attached to the oscillator head and bolted onto the vacuum system. The sample chamber is pumped to the 10^{-10} psia (10^{-6} Pa) range with the sample at about 71.6°F (22°C), and the oscillator mass is zeroed after the mass loss or gain has equilibrated. The system temperature is equilibrated to 71.8°F (22.1°C), and water is admitted to the samples to a pressure of 0.0193 psia (133 Pa). The system is allowed to equilibrate (both pressure and mass measurements). The water vapor pressure is then increased to about 0.0388 psia (266 Pa) and then in increments of 0.0388 psia; pressure and mass measurements are taken

TABLE 1

Polymers Characterized for Water Vapor Sorption Performance

Acronym	Source	Polymer	Comments
AMBH	Polysciences, Inc. Cat. #4698	amberlite IR-120 H form	
CA	Aldrich Chem. Co. Cat. #18,095-5	cellulose acetate	
CSSS	Scientific Polymer Prod., Inc. Cat. #023	cellulose sulfate sodium salt	
MC	Scientific Polymer Prod., Inc. Cat. #144	methyl cellulose	MW 86,000 (GPC)
N	Scientific Polymer Prod., Inc. Cat. #033	nylon 6',6	Crosslinked; could not be studied with QCM
PAA	Scientific Polymer Prod., Inc. Cat. #598	polyacrylic acid	MW 3,000,000
PAAAS	Polysciences, Inc. Cat. #3311	polyacrylic acid ammonium salt	MW 250,000
PAASS	Scientific Polymer Prod., Inc.	polyacrylic acid sodium salt	
PACM	Scientific Polymer Prod., Inc. Cat. #376	polyacrylamide-carboxyl modified	MW 200,000
PBM	Polysciences, Inc.	poly(butylmethacrylate)	
PC	Scientific Polymer Prod., Inc. Cat. #035	polycarbonate	MW 20-25,000
PEG	Scientific Polymer Prod., Inc. Cat. #491	polyethylene glycol	MW 6800
PEMAASS	Polysciences, Inc. Cat. #16271	poly(ethylene-methacrylic acid) sodium salt	
PEO	Scientific Polymer Prod., Inc. MW 100,000-Cat. #136A	polyethylene oxide	Studied with MW 3,400; 18,000; and 100,000. (All from STD-3 kit)
PFSA	duPont	perfluorosulfonic acid	duPont Nafion Type NR50
PHMA	Polysciences, Inc. Cat. #6557	poly(hexamethylene) adipamide	
PMAASS	Polysciences, Inc. Cat. #0503	poly(methacrylic acid) sodium salt	MW 15,000
PSMQ	Scientific Polymer Prod., Inc. Cat. #715	polystyrene, crosslinked, mixed quartenary ammonium (hydroxide form) and sulfonic acid (H form)	
PSSASS	Polysciences, Inc. Cat. #8773	polystyrenesulfonic acid sodium salt	Available in both water soluble form and crosslinked beads. The latter could not be studied with the QCM. MW 500,000 (powder)
SPSS	Scientific Polymer Prod., Inc. Cat. #'s 619, 623, 625, 628	sodium polystyrene sulfonate	MW 178,000 (#625) MW 60,000 (#623) MW 4,600 (#619) MW 1,200,000 (#628)
PVAVSSS	Polysciences, Inc. Cat. #15662	poly(n-vinylacetamide, vinyl sulfonate) sodium salt	
PVP	Scientific Polymer Prod., Inc. Cat. #328	polyvinylpyrrolidone	MW 10,000
PVSASS	Polysciences, Inc. Cat. #4392	poly(vinylsulfonic acid) sodium salt	MW 2,000
PVSPS	Aldrich Cat. # 27,196-9	poly(vinyl sulfate) potassium salt	

during the approach to equilibrium and after equilibrium is reached at each pressure. After reaching the desired maximum pressure—0.310 psia (2.133 kPa) in this work— the process is reversed by decreasing the water vapor pressure in about 0.0388 psia (266 Pa) decrements followed by equilibration intervals. There is no design restriction for making pressure changes of about 0.0388 psia (266 Pa), which were chosen for our convenience; any desired pressure change can be chosen up to 0.310 psia (2.133 kPa) at 71.8°F (22.1°C). Higher pressures can be studied by increasing the ambient temperatures of the *entire* QCM and vacuum apparatus.

In general, data for the first isotherm determination were obtained at about 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, and 80% RH by increasing the water vapor pressure from a vacuum of less than about 10^{-9} psia (10^{-5} Pa) to an initial pressure of about 0.0193 psia (133 Pa) (5% RH) and monitoring the uptake for about 45 minutes. The capacity changes reported in the isotherms for all polymers are relative to the sample mass after evacuation at 71.8°F (22.1°C). The percent of water uptake is calculated by multiplying the area of polymer times the mass of water gained (or lost) times 100% and dividing by the mass of the polymer on the crystal. The percent water vapor uptake is given by % $H_2O = 7.85\ d^2\ (\Delta m)/M$, where d is the diameter in mm of the polymer coating on the QC, Δm is the change in ng/cm^2 of the QCM readings between vacuum and at any water vapor pressure, and M is the sample mass in µg. M can be corrected for the loss during outgassing by using $M = M_0 - \pi d^2 \Delta m_0/4$, where M_0 is the sample mass measured in air and Δm_0 is the ng/cm^2 loss during outgassing. The factor 0.0785 d^2 results from the polymer coating covering a larger area than the sensing area (58 mm^2) of the QC that yields the mass reading in ng/cm^2. This factor then corrects the polymer mass (M) to the fraction of M that is coating the sensing area of the QC. The maximum value for d is 14 mm, the diameter of the crystals used in this work. The actual value for d, which is obtained by combined visual and optical inspection of the polymer coating, has typically ranged between 12 and 13 mm.

The percent of relative humidity is calculated by multiplying the capacitance manometer pressure reading times 100% and dividing by the saturation pressure of water at the system temperature. These calculations have been simplified by carrying out our sorption studies at 71.8°F (22.1°C) where the saturation vapor pressure of water is taken as 0.38674 psia (2.666 kPa or 20.0 torr). The actual vapor pressure at 71.8°F (22.1°C) is 0.038577 psia (2.660 kPa). Thus, each 0.019337 psia (133.3324 Pa or 1 torr) corresponds to 5% in RH, where RH is the most widely used representation of the partial pressure of water in desiccant cooling research, development, and applications.

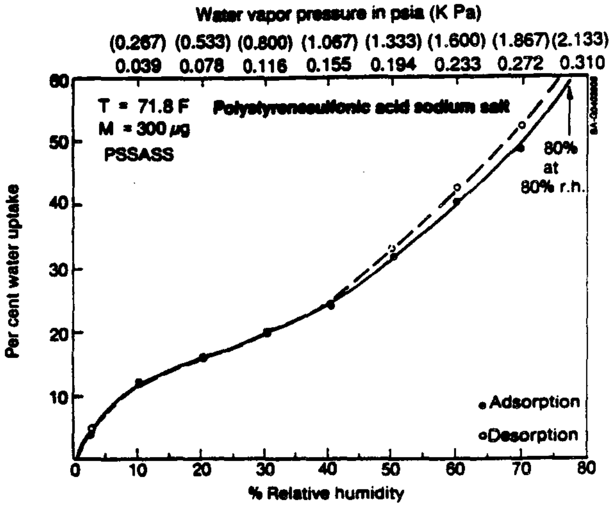

Figure 2 *Water vapor sorption isotherm for PSSASS at 71.8°F (22.1°C)*

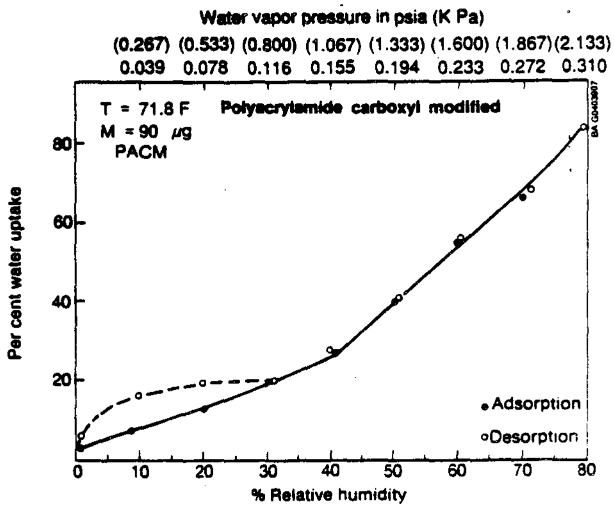

Figure 3 *Water vapor sorption isotherm for PACM at 71.8°F (22.1°C)*

EXPERIMENTAL RESULTS

Isotherms of Polymers Studied

Of the criteria for a candidate ADM, the determination of an adsorption isotherm provides four important pieces of data: (1) the shape, (2) the capacity and possible capacity change between 5% and 60% RH, (3) the absence or presence of hysteresis between the adsorption and desorption legs of the isotherm, and (4) the kinetics of the sorption or desorption process after each pressure change.

Five of the isotherms determined with the QCM apparatus are shown in Figures 2 through 6. These are all type II isotherms that approach the type I, moderate shape (Collier 1986) if RH from 5% to 60% is primarily considered. In Figure 7, we have redrawn the type I,

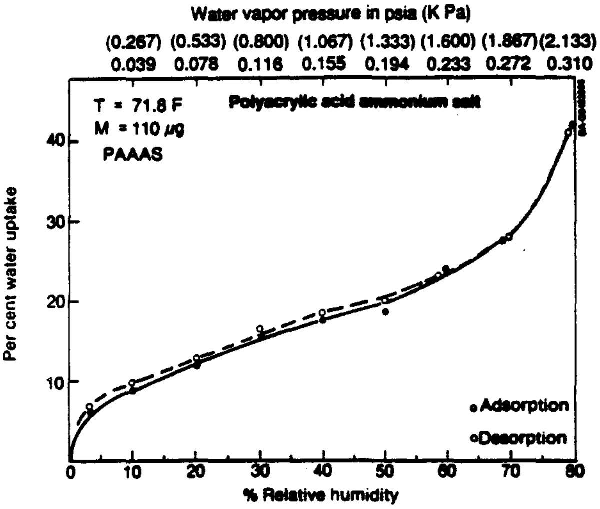

Figure 4 *Water vapor sorption isotherm for PAAAS at 71.8°F (22.1°C)*

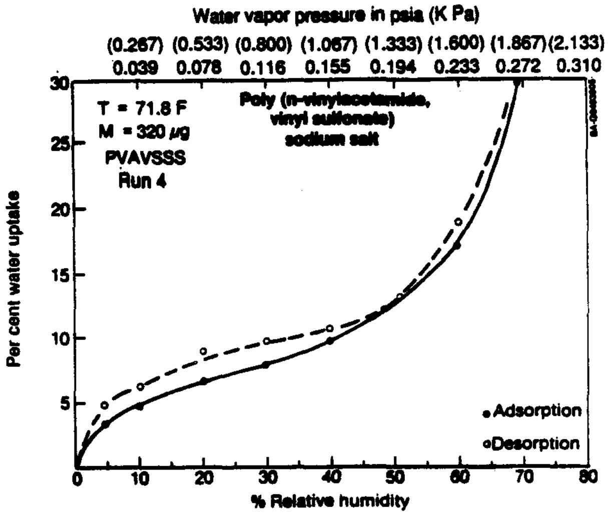

Figure 5 *Water vapor sorption isotherm for PVAVSSS at 71.8°F (22.1°C)*

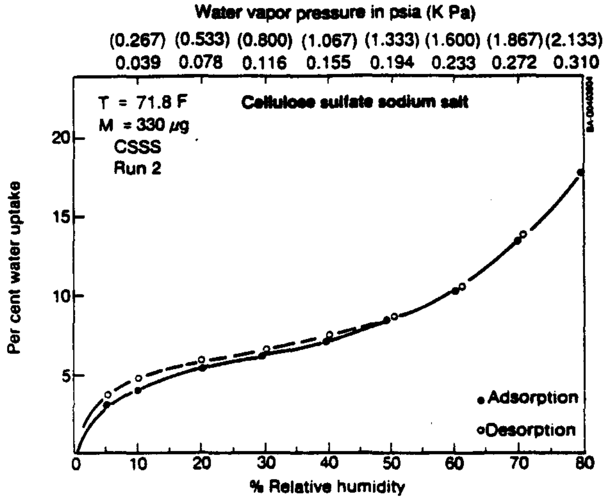

Figure 6 *Water vapor sorption isotherm for CSSS at 71.8°F (22.1°C)*

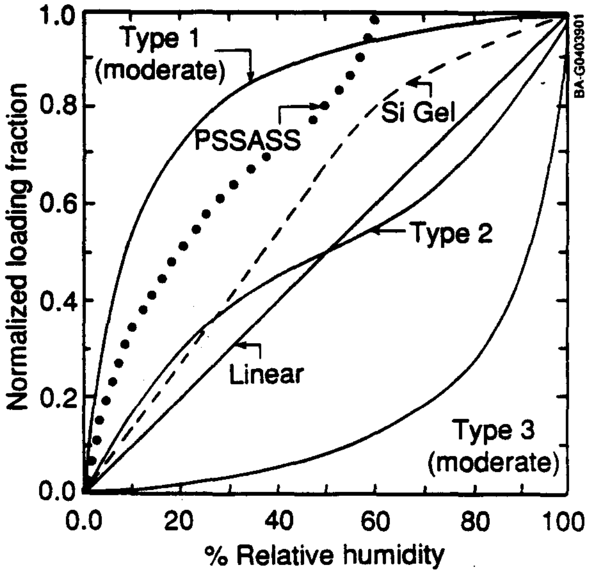

Figure 7 *Comparison of PSSASS and silica gel isotherms with Collier's Type I, moderate; Type II, linear; and Type III, moderate isotherms (Collier 1986)*

moderate; type II; type III, moderate; and linear isotherms used for the computer parametric study (Collier 1986). We have also plotted the isotherm for a silica gel, where the 37% water uptake at 100% RH is normalized to a loading fraction 1.0 and part of the isotherm for PSSASS, where the 40% water uptake at 60% RH is normalized to a loading fraction of 1.0. Similar comparisons made with the data from Figures 2 through 6 yield similarly inflected curves that fall between the PSSASS and type II curves. The sample mass given on each figure is the mass measured in air and uncorrected for losses on outgassing. The isotherms shown have a favorable (but not ideal) isotherm shape, capacity, absence of hysteresis, and rapid kinetics of adsorption and desorption and are considered to be most promising candidate ADM. The isotherms of the remaining polymers have been presented (Czanderna 1988). All but four of these polymers are not considered interesting as ADM for DCS. Brief comments about the isotherm for each polymer that provide the rationale for continuing to include the polymers for further study as *candidate* ADM or for not including them in this category are given in Table 2.

TABLE 2

Summary of Isotherm Data for 23 Polymers Studied as Potential Advanced Desiccant Materials

Polymer No.	Acronym	Fig. No.	Mass. (μg)	Isotherm Type	% Capacity at 80% R.H.	Capacity Change from 5% to 60%	Hysteresis	Kinetics	Other Comments
1.	PASSASS	2	300	2	80	31	Above 50% R.H.	Fast	Excellent repeatability on numerous multicycle runs.
2.	SPSS		440	2	60	21	Yes	Fast	Hysteresis disappeared on run 4; capacity dropped from 60% to 30%.
3.	PACM	3	90	2 or 3	85	45	Yes, low R.H.	Slow, low R.H.	Husteresis occurs only below 30% R.H. accompanied by slow kinetics.
4.	PAAAS	4	110	2	42	17	Yes	Fast	Hysteresis becomes less pronounced with cycling; capacity decreases by a factor of 2 through 4 cycles.
5.	PMAASS		370	2	43	22	Negligible	Fast	Hysteresis decreases on cycling; capacity increases slightly through 4 cycles.
6.	PVAVSSS	5	320	2	40 + Exp.	13	Yes	Fast	Hysteresis maintained on cycling; capacity increases from 1 through 4 cycles.
7.	PAASS		350	2	26	9	Yes	Fast	Hysteresis mantained through 4 cycles; no change after 2nd cycle.
8.	CSSS	6	330	2	18	7	No	Fast	Negligible hysteresis and capacity change through 4 cycles.
9.	MC		440	2	20	10	Yes	Fast	Stabilized for runs 2 and 3; desorption erratic in run 1.
10.	PVP		110	3	13	5.5	Yes	Fast	Hysteresis minimal; isotherm is at crossover from type 2 to 3.
11.	PAA		305	2	7	2.6	Yes	Fast	Compare hysteresis with PAASS PAAAS.
12.	PEO		110	3	4	1.5	Yes	Fast	Severe hysteresis at MW's of 3,400 and 100,000 as well. All type 3. Data taken up to 90% R.H., which is the cause for hysteresis at just below 80% R.H.
13.	PEG		430	3	2+	1	Yes	Fast	No Comments
14.	PVSPS		170	3	6	2	Yes	Fast	No Comments
15.	PFSA		70	3	3	2+	Yes	Slow	No Comments
16.	PHMA		110	2	1.2	0.7	Yes	Fast	No Comments
17.	PVSASS		440	3	1.2	0.5	Yes	Fast	No Comments
18.	PSMQ		360	1M	1.2	0.9	Yes	Fast	Isotherm is nearly ideal as ADM; capacity change is low.
19.	AMBH		320	3	0.55	0.25	Yes	Fast	Capacity was only 1% maximum on run 1.
20.	CA		180	3	1.2	0.4	Yes	Fast	Unusual behavior between 40% and 60% R.H. not understood. Desorption data incomplete.
21.	PBM		300	3	0.6	0.5	Yes	Fast	Capacity increased from runs 1 to 3.
22.	PC		500	—	0.4	—	—	Slow	Capacity determined at 80% R.H. only.

Kinetics of Sorption and Desorption by Candidate ADM Polymers

After each pressure increment or decrement while obtaining the isotherm data, the approach to the equilibrium mass gain or loss was recorded at two-minute intervals through the first 20 minutes and then at 10-, 20-, or 30-minute intervals for 4 to 6 hours. In the semi-automatic operational mode of the QCM, these data are printed but are not plotted for visual display or interfaced to a graphics terminal. Qualitative statements of fast, intermediate, and slow were assigned after visual inspection of the data. These statements are listed in Column 7 of Table 2. The definitions are as follows: fast, more than 90% of the incremental or decremental mass change occurred in the first 10 minutes; intermediate, more than 90% of the mass incremental or decremental change occurred in the first 60 minutes; and slow, less than 90% of the incremental or decremental mass change occurred during the first 60 minutes. For commercial desiccant cooling systems (CDCS), only fast kinetics will qualify a material as a

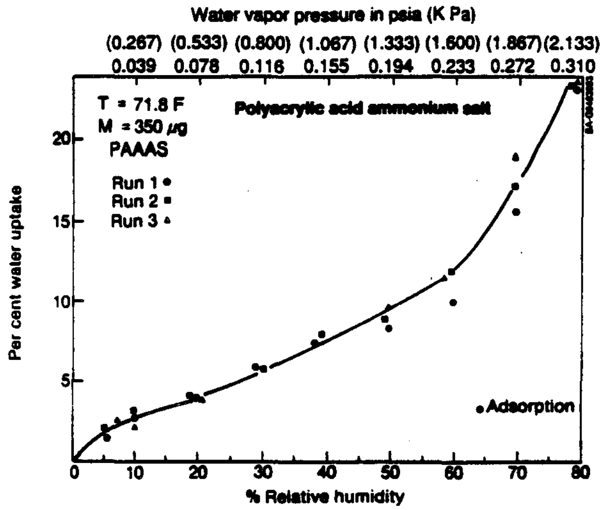

Figure 8 *Water vapor sorption isotherms for PAAAS at 71.8°F (22.1°C) (three cycles)*

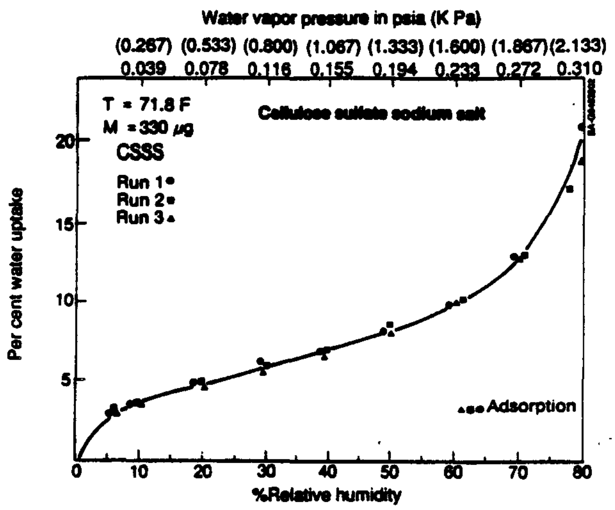

Figure 9 *Water vapor sorption isotherms for CSSS at 71.8°F (22.1°C) (three cycles)*

candidate ADM. Intermediate kinetics do not necessarily disqualify a material as a candidate, and slow kinetics probably disqualify a material.

Cyclic Stability Studies

A candidate ADM must exhibit reproducible sorption behavior after being subjected to several tens of thousands of adsorption and desorption cycles. From our study of the literature, major changes in the sorption behavior of many polymers occur in the first one or two cycles. Repeated measurements of sorption isotherms have not been undertaken in previous work given in the literature or in this research. We have subjected several polymers to three to nine sorption cycles by simply remeasuring the isotherms. Typical results for the cyclic adsorption and desorption of water vapor are shown for PAAAS and CSSS in Figures 8 and 9 for the first three cycles. As is seen, the cyclic reproducibility is excellent for the first three adsorption cycles (similar desorption data were obtained). In contrast, similar adsorption data for four cycles of PEO show dramatic changes in adsorption behavior from the first to second cycle, and continuing changes for the next two cycles. The changes quite likely result from physical processes occurring within the polymer because of the adsorption and desorption cycles.

DISCUSSION

The results shown in Figures 2 through 6 and Figures 8 and 9 were selectively chosen based on performance criteria developed early in this research. First there are potential candidate ADM that fall within broad guidelines for an ADM, but have been inadequately characterized to meet the performance criteria of an ADM. Secondly, there are the performance criteria that must be met to become a candidate ADM. Both of these sets are discussed below. Even when a material reaches candidate ADM status, it must be thoroughly studied before it can be elevated to the status of a test ADM. In this paper, we have conducted screening experiments to narrow a list of potential candidate ADM to candidate ADM.

Criteria Used for Ranking Potential Candidate Materials

Of the two sets of parameters that could be applied for ranking the materials identified in our literature search as a list of potential candidate ADM, the first set is as follows: (1) cost, both initial and life-cycle; (2) performance; (3) durability, lifetime, and how performance parameters depend on temperature; (4) availability; (5) processability; (6) modifyability; (7) stability at temperatures below 100°C; and (8) specific heat. For polymeric materials, the most important initial criterion is performance. As a first approximation, polymers should have relatively uniformly good prospects for cost, availability, processability, modifyability, and stability and marginal values for specific heat. It was *not* expected that durability of polymers used as desiccants would have been evaluated, and this expectation is correct (Czanderna and Thomas 1986).

Performance Criteria for Candidate Advanced Desiccant Materials

The second set of parameters considered are performance related and were divided into three categories: primary, secondary, and other criteria. These criteria were ranked and reviewed by several members of the SERI desiccant team before they analyzed the available literature references. The criteria, which are more detailed than previous listings, were generated by SERI researchers in 1985 (Czanderna and Thomas 1986). These now must be modified because of a recent computer parametric study (Collier 1986). The modified criteria listed below are subjectively based on a combination of input obtained by the author from several sources.

Primary criteria for further narrowing the potential of polymeric materials as advanced desiccants are as follows:

1. Isotherm shape (Type I, moderate, as defined by Collier [1986]). Silica gel has a linear-type isotherm, which results in an upper limit of 1.05 for the thermal COP. See Figure 7.

2. Capacity *change* of at least 6% to 8% by weight between 5% and 60% RH. Note that large capacities are not nearly as important as previously thought, which not only enlarges the list of polymeric potential ADM, but also of inorganic materials as well.

3. Rapid adsorption at 71.6°F (22°C). Rapid is interpreted to mean that most of the capacity change must be completed in less than five minutes to correspond to the anticipated exposure time in rotary CDSC.

4. Reversibility on desorption at 71.6°F (22°C) for isotherm determination. Rapid desorption rates are helpful but not necessary because the desorption kinetics will be increased by elevated regeneration temperatures.

5. Reproducibility in criteria 1 through 4 above following regeneration up to 176°F (80°C); i.e., the *present* anticipated regeneration temperature for solar-based DCS. If higher regeneration temperatures are planned, then the 176°F (80°C) must be increased accordingly.

Secondary criteria that eventually need to be applied to materials passing the above criteria include:

6. Diffusivity of greater than 10^{-8} ft^2/s (ca. 10^{-9} m^2/s). Qualitative aspects of diffusivity or permeation rates are automatically observed during studies with QCM and beam microbalance techniques from criteria 3 and 4 above.

7. Desorption rates of water at the regeneration temperature that provide sufficient capacity change in less than five minutes.

8. Heats of adsorption at or near 2508 kJ/kg, which is the latent heat of vaporization of water. Higher heats of adsorption result in a decrease in overall DCS efficiencies.

9. Specific heats with $(dw/dx)/C_p$ greater than 0.5 gK/J for 5% to 80% RH. This parameter is now thought to be less important than in 1985 and, in fact, does not have a wide range of variability for polymers.

Other criteria, which then need to be applied to materials that remain candidates after applying 1 through 9, include cyclic stability, durability in pure water, synthetic-air environments, and life-cycle costs that are competitive, with or without contamination by use in working environments.

Since the goal of our research is to measure the performance parameters of the material itself in pure water vapor, the obvious engineering-related parameters (e.g., bed geometry, material form, desiccant size and shape, packing density, pressure drops, heat and mass transfer, and gas-side diffusion effects) were not considered but could easily be factored into future concepts. Adsorbing water vapor from an airstream rather than from pure water vapor will only change kinetics and not the isotherms as determined with QCM. The candidate ADM listed in the conclusion section have been determined by applying criteria 1 through 4 above. Further study of these materials is warranted to determine if any of them should be subjected to engineering test configurations.

Accuracy and Limitations of QCM Apparatus

The advantages and limitations of using the QCM apparatus for studies of ADM were understood prior to deciding to construct the equipment. Most of the results obtained and presented in this paper have been efficiently obtained because of the advantages of the QCM apparatus. The limitations concerning the sample size, accuracy, and types of materials that can be studied and the need for further improvements have been discussed (Czanderna 1988).

The QCM has a fundamental limit of 10 mg for the polymer sample mass based on the design of the control unit and the cut of the crystal for operation at 6 MHz. Our experience has been that a practical limit of less than 1 mg apparently is imposed by polymers with a large sorption capacity. When polymers reach sorption capacities of more than 20% to 40%, depending on the polymer, the apparatus indicates "fail." The reason for "fail" in this case probably results from the polymer plus sorbed water changing its behavior from a solid to a "liquid-like" material at the largest sorption capacities. Isotherm determination is lost from the pressure where a "fail" is obtained and at all higher pressures. These data could be routinely obtained by incorporating a beam microbalance into the present apparatus.

The accuracy of the QCM data (i.e., the sorption capacity and kinetics of capacity changes) is limited by two principal uncertainties. The first is the sample mass itself. The sample mass is determined by weighing a QC before and after coating it with a polymer. Each weighing is now limited to ± 5-10 µg so the uncertainty for the sample mass determination depends on the difference between two large numbers or ± 10-20 µg for a single weighing. This limits the accuracy of the sample mass to 10% to 20% for a 100-g sample or 2% to 4% for a 500-g sample, which are the typical sample masses studied thus far. There are several solutions to the limitation on accuracy imposed by the value of sample mass. These are: (1) to adopt statistical procedures for repeated weighing of the QC with and without polymer, (2) to purchase a microbalance that has a weighing precision of 1 µg or better, and (3) to study much larger samples, as would be the case with a beam microbalance.

Finally, the most serious limitation to using the QCM is that samples must be adherently mounted onto a QC. Polymers that cannot be dissolved, that are highly cross-linked polymers or cast as films, etc., are difficult or impossible to study with the QCM because they cannot be mounted on a QC. All the forms of polymers anticipated as potential ADM can be studied using beam microbalance techniques.

CONCLUSIONS

Our work has provided a rapid QCM method for evaluating the performance properties of ADM with an emphasis on polymers. These include measuring sorption isotherms, sorption and desorption kinetics, and the cyclic stability of ADM. By considering performance criteria desired for ADM, we have narrowed the number of commercially available polymers to nine candidate ADM for further study and/or modification. These are:

—polystyrenesulfonic acid sodium salt	(PSSASS)
—sodium polystyrene sulfonate	(SPSS)
—polyacrylamide-carboxyl modified	(PACM)
—polyacrylic acid ammonium salt	(PAAAS)
—poly(methacrylic acid) sodium salt	(PMAASS)
—poly(n-vinylacetamide, vinyl sulfonate) sodium salt	(PVAVSSS)
—polyacrylic acid sodium salt	(PAASS)
—cellulose sulfate sodium salt	(CSSS)
—methyl cellulose	(MC)

Of these, PSSASS, PAAAS, and CSSS appear to be of special interest because of performance properties measured thus far. In the future, additional polymers need to be studied that are modifications of those commercially available or synthesized specifically to serve as an ideal desiccant. Eventually, those polymers with the best properties must be subjected to simulated and/or actual use conditions, and causes for any performance loss need to be identified. Clearly, the polymers we have characterized can be placed in presently designed DCS that are in commercial use or being used to test the properties of desiccants.

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This research is concerned with solid materials used as desiccants for desiccant cooling systems (DCSs) that process water vapor in an atmosphere to produce cooling. Background information includes an introduction to DCSs and the role of the desiccant as a system component. The water vapor sorption performance criteria used for screening the modified polymers prepared include the water sorption capacity from 5% to 80% relative humidity (R.H.), isotherm shape, and rate of adsorption and desorption. Measurements are presented for the sorption performance of modified polymeric advanced desiccant materials with the quartz crystal microbalance. Isotherms of PSSA taken over a 5-month period show that the material has a dramatic loss in capacity and that the isotherm shape is time dependent. The adsorption and desorption kinetics for PSSA and all the ionic salts of it studied are easily fast enough for CDCS applications with a wheel rotation speed of 6 min per revolution. Future activities for the project are addressed, and a 5-year summary of the project is included as Appendix A.

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