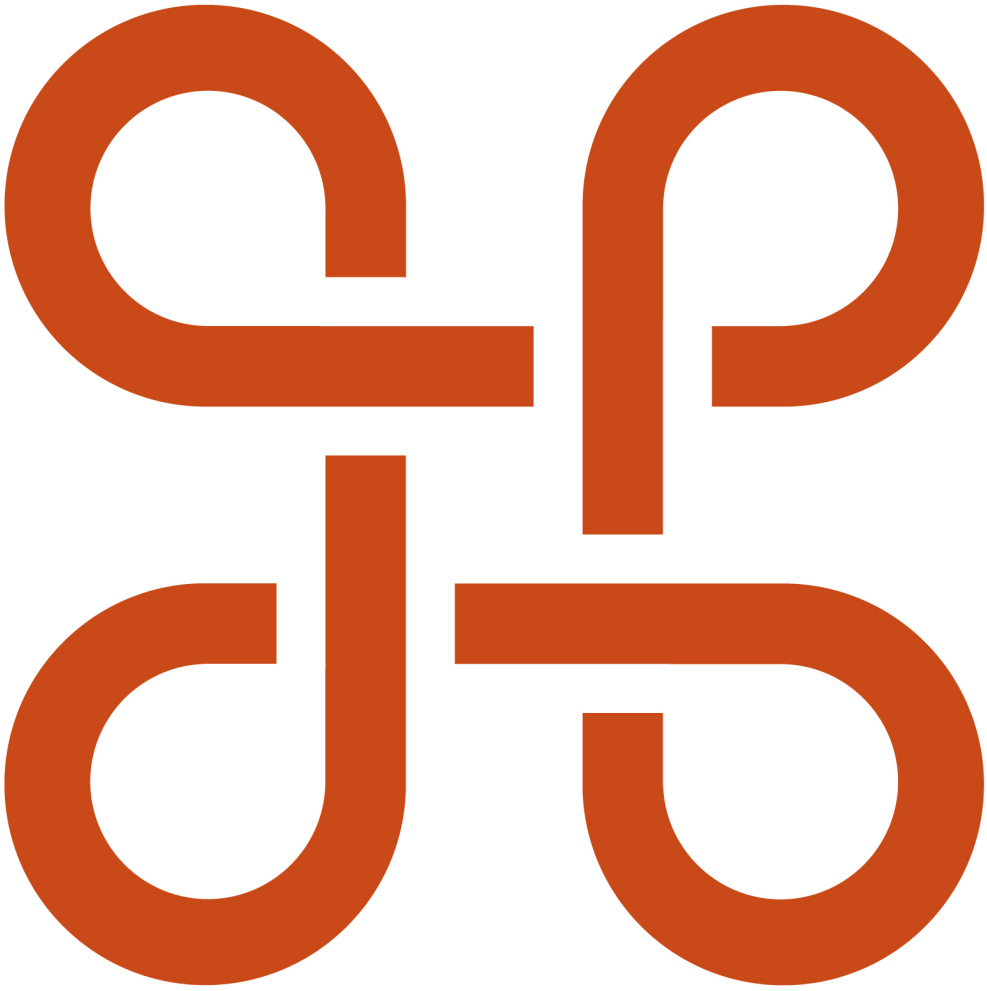
Adsorbents for Pollution Reduction in Cultural Heritage Collections



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Contributors

The contents of this report were designed and written by Elyse Canosa with support from Sara Norrehed, both project advisors at the Swedish National Heritage Board (Riksantikvarieämbetet). Anders Karlsson and Andreas Fischer performed experiments at Research Institutes of Sweden (RISE) in Borås, Sweden. Charlotta Rigbrandt performed experiments at the Camfil Tech Center in Trosa, Sweden. Further consultation at Camfil was provided by Chris Ecob, Mikael Eriksson, and Mikael Forslund. The case study at Visby Landsarkivet was made possible through collaboration with Cia Hipfl, Jan Östergren, and Madelene Nettermark. Finally, Marta Segura Roux at the Swedish Environmental Research Institute (IVL) provided valuable practical information throughout the project.

Svensk sammanfattning

Denna rapport handlar om grundläggande principer och praktisk information kring adsorbenter och deras användning inom kulturarvsinstitutioner. Luftföroreningar kan produceras både utomhus och inomhus. Till exempel kan avgaser leta sig in i byggnader via fönster, sprickor och ventilationssystem. Luftföroreningar som uppkommer inomhus avges framförallt ifrån byggnadsmaterial, inredning, människor, restaurangverksamhet och maskiner. Luftföroreningar påverkar luftkvaliteten negativt och kan vara skadliga för människor, föremål och försvårar samlingsförvaltning. Det finns många sätt att minska mängden luftföroreningar, ett av dessa är att använda adsorbenter. Adsorbenter är porösa material som har förmågan att attrahera gasformiga ämnen till sin yta. Adsorbenter används ofta för luftrening i moderna ventilationssystem. De vanligaste adsorbenterna är aktivt kol, silikagel, zeoliter och polymerbaserade material. De olika typerna har specifika egenskaper och används vid olika situationer där luftrening behövs. Denna rapport förklarar grundläggande begrepp som är användbara för att förstå egenskaperna hos olika adsorbenter. I rapporten finns också beskrivningar av de vanligaste och kommersiellt tillgängliga adsorbenterna, deras egenskaper och användning. Genomgående i rapporten lyfts och diskuteras tillgänglig litteratur som kan vara till hjälp för konservatorer och samlingsförvaltare i processen för att förbättra luftkvaliteten i samlingar.

Förutom den generella översikten av adsorbenter presenterar denna rapport en jämförande studie av fyra adsorbenter; tre olika zeoliter samt aktivt kol. Mycket lite forskning finns tillgänglig som jämför adsorbenter under de förutsättningar som råder på museer. Sådana speciella förutsättningar är till exempel lågt luftflöde, låga koncentrationer av luftföroreningar som inte är skadliga för människor men för föremål, samt låg–medel luftfuktighet. Med hänsyn till dessa omständigheter jämför studien adsorptionsförmågan hos vanliga zeoliter och aktivt kol, vilket ger en inblick deras potential för användning inom kulturarvsinstitutioner. Resultaten indikerar att aktivt kol generellt adsorberade effektivare än zeoliterna, men att zeoliter kan vara effektivare under vissa förhållanden, som i mycket torra miljöer.

Rapporten vänder sig till läsare som har nytta och intresse av den vetenskapliga aspekten för användningen av adsorbenter på kulturarvsinstitutioner. Detta inkluderar, men begränsas inte till, konservatorer, samlingsförvaltare och forskare inom konservering och heritage science. Rapporten är sammanfattad i enkla praktiska råd genom en serie *Vårda väl-blad* som finns tillgängliga via Riksantikvarieämbetet, www.raa.se/vardaval.

Abstract

This report discusses the basic principles and practical implementation of adsorbents, framing the information for cultural heritage environments. Pollutants exist in all cultural heritage environments. These pollutants can be produced outdoors or indoors. Outdoor pollutants, such as smog, may enter buildings through windows, cracks, and ventilation systems. Indoor pollutants are produced by construction and decoration materials, people, food preparation, and appliances. Such pollutants affect air quality, posing risks to both human health and cultural heritage preservation. There are many ways to reduce or control pollutants; one of these methods is through using adsorbents. Adsorbents are highly porous, rigid materials that collect gas particles by surface adhesion, a process known as adsorption. They are often used for air filtration and can be applied to cultural heritage environments. The most common commercial adsorbents are activated charcoal, silica gel, activated alumina, zeolites, and polymer-based adsorbents. Each type of adsorbent has its own distinct properties and can be applied to different air quality situations. This report presents and defines common terminology such as physisorption, chemisorption, desorption, and capacity, all of which are useful for understanding the capabilities of adsorbents. There is also information about the five most common commercial adsorbents, their properties, and their uses. Such properties include affinity for water, pore sizes, adsorption mechanism, and chemical composition. Throughout this document, existing literature on the use of different adsorbents in cultural heritage environments is discussed. Such information can help conservators and collection managers make scientifically supported decisions to improve and control air quality in collections.

In addition to general adsorbent information, this report presents a study comparing four adsorbents: three different zeolites and one type of activated charcoal. Little research exists that compares different zeolites under typical museum conditions. Such conditions include low airflow, low pollutant concentration, room temperature, and moderate humidity. Additionally, some pollutants like acetic acid are a large concern for cultural heritage collections but are of much less concern for human health. Using these considerations, this study compares the adsorption capabilities of common zeolites exposed to acetic acid gas and offers insight into their potential use in cultural heritage environments. Three different experimental processes were used. The adsorbents were exposed to acetic acid and formic acid gas under forced airflow in collaboration with Camfil, an air filtration company in Trosa, Sweden. At Research Institutes of Sweden (RISE), the adsorbents were placed in headspace vials with acetic acid gas and allowed to adsorb passively without forced airflow. The amount of acetic acid gas in the vial was analyzed using gas chromatography – mass spectrometry (GC-MS). Finally, a case study was performed using a cellulose acetate photographic negative collection at Visby Regional State Archive (Visby Landsarkivet). The concentration of acetic acid gas in negative storage boxes was measured before and after the installation of adsorbents using passive air samplers from the Swedish Environmental Research

Institute (IVL). The results indicated that activated carbon performed better than all three zeolites, but that zeolites may have applications in certain heritage environments, such as those requiring very dry environments.

This report is intended for readers with an interest in the scientific aspects of air quality control via adsorbents in cultural heritage collections. This can include (but is not limited to) collection managers, museum conservators, and conservation scientists. The literature and concept review of adsorbents is presented in a way that does not require technical knowledge. Some technical knowledge about gas phase analysis is helpful in interpreting the results from the experimental study. Shorter, practical, and non-technical documents in Swedish have been adapted from this report and are available through Riksantikvarieämbetet's *Vårda väl-blad* series, www.raa.se/vardaval.

Introduction

A primary concern for indoor cultural heritage collections is air quality. Such a concern is important for human health and collection preservation. Pollutants that are generated both outdoors and indoors are found in all cultural heritage buildings. Cultural objects can react to pollutants, resulting in corrosion, fading, and embrittlement among other deterioration mechanisms. There are a number of ways to reduce pollutants in collections, one of which is through the use of adsorbents. Adsorbents are highly porous materials that capture ions, molecules, or atoms from a surrounding medium (i.e. liquid, gas) through surface adhesion. They are commonly used to purify water and air. In cultural heritage contexts, adsorbents are often placed inside display cases, storage containers, portable air purifiers, or HVAC (heating, ventilation, and air conditioning) systems. There are many types of adsorbents, and one can choose from a range of properties or capabilities. This report intends to discuss several classes of adsorbents, including activated carbon, activated alumina, silica gel, zeolites, and polymeric adsorbents. These materials will be reviewed in terms of their physical and chemical properties, adsorption mechanisms, and practical uses, framing the information for cultural heritage contexts. In addition to a review, this report also presents an experimental investigation into three different zeolites (4A, 5A, 13X) and activated carbon. The study focuses on their behavior when exposed to acetic acid and formic acid gases.

The major pollutants of concern for cultural heritage environments include sulfur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3), hydrogen sulfide (H_2S), formic acid (HCOOH), and acetic acid (CH_3COOH). Pollutants that have outdoor sources (e.g. biological processes, industrial processes, automobile combustion) include SO_2, NO_x, and O_3. They can pass through windows, doors, and other openings in buildings. Additionally, they can be drawn into the building by the ventilation system. In cultural heritage environments, outdoor pollutants are often found in galleries or storage rooms. Pollutants that are produced by indoor sources (e.g. construction or decoration materials, cooking, appliances) include SO_2, NO_x, O_3, H_2S, formic acid, and acetic acid. While it is possible to protect collection objects from outdoor pollutants by placing them inside display cases or storage containers, materials inside these containers may also produce harmful pollutants. It is therefore important to consider methods for reducing pollutants in all display, storage, and packing conditions. Other problematic pollutants for heritage collections include carbonyl sulfide (COS), hydrogen chloride (HCl), peroxides, ammonia (NH_3), acetaldehyde (CH_3CHO), formaldehyde (CH_2O), and piperidinol-based compounds. Further information on gaseous pollutants in museum environments and their effects on cultural heritage are available through several comprehensive reviews (Grzywacz 2006, Tetreault 2003, Brimblecombe 1990, Watt, et al. 2009, Hatchfield 2002). If any such pollutants are detected or suspected in a collection environment, adsorbents can be used to reduce their concentrations. Other methods of reducing pollutant concentrations include choosing indoor materials that do not produce harmful gases, blocking the source of the pollutant by

introducing barrier layers, and increasing airflow between the source and a space with lower pollutant concentrations.

Adsorbents are named such because they work via adsorption, i.e. the process of ions, atoms, or molecules adhering to a surface. Adsorption must not be confused with absorption, a process in which ions, atoms, or molecules permeate into the bulk of a material. A substance that adheres to the surface of an adsorbent is called the adsorbate. Desorption is the opposite process of adsorption as it is the process of a substance releasing from a surface. Although all surfaces experience some level of adsorption, materials that are considered "adsorbents" have very large surface areas due to their high porosity. They provide many sites on which adsorption can occur. These materials can therefore capture and retain large amounts of substances that pass through them. Although adsorbents can collect gas and liquid substances, this report will focus on gas-phase adsorption, as it is most significant for cultural heritage applications.

Employing adsorbents for their useful surface properties is not a recent phenomenon. The ancient Egyptians, Greeks, and Romans used adsorbent materials like clay and wood charcoal to treat diseases and desalinate water (Rouquerol, et al. 2014). Descriptions of scientific experiments to understand adsorption phenomena date back as far as 1230 B.C. (Robens and Jayaweera 2014). Scientific interest in adsorbents substantially increased in the 18th century, beginning with publications by Fontana and Scheele in 1777. They performed quantitative studies of gas uptake by charcoal and clay (Fontana 1777, Scheele 1777). While adsorbents were investigated throughout the 19th and 20th century, major commercial developments for activated carbon occurred during World War I when it was used to remove toxic chemicals from air (Yang 2003). Since then, adsorbents have been used extensively for commercial and research purposes, and new types of adsorbents are constantly in development. This review will focus on the most widely available adsorbents: activated carbon, activated alumina, silica gel, zeolites, and polymer-based adsorbents. These materials are the most likely to be used in cultural heritage environments as they are commercially accessible, affordable, and highly researched. Some recent developments in adsorption technology will also be briefly touched upon, including metal organic frameworks (MOFs), carbon molecular sieves, and structural adsorbents.

Like other disciplines that use adsorbents, heritage preservation has its own set of needs. Some desirable properties of adsorbents in cultural heritage environments include that they should:

- Maintain low pollutant concentrations
- Work effectively in low airflow situations
- Not affect humidity levels strongly
- Be affordable
- Be reusable
- Provide long-term effectiveness
- Be chemically stable / not harm collection objects

- Not desorb harmful pollutants
- Release minimal dust or fine particles

Collection environments typically require very low pollutant concentrations as cultural materials can be highly sensitive to specific pollutants. For example, silver objects tarnish when exposed to hydrogen sulfide at parts per trillion (ppt) concentrations (Watts 2000). In comparison, hydrogen sulfide found in typical ambient conditions are much higher, approximately between 0.1 and 0.3 parts per billion (ppb) (Chou 2003, US EPA 1993). Industrial applications of adsorbents often deal with much higher concentrations of gaseous compounds (on the parts per million, ppm, level or higher). Experimental tests of adsorbents therefore typically use high gas concentrations that may not easily translate to cultural heritage contexts. Collection environments also generally have low airflow, particularly in enclosed spaces such as display cases or storage containers, unless a fan or air pump is installed. Situations that do not force the movement of air are referred to as "passive". If adsorbents are incorporated into a portable air purification unit or an HVAC system, air is forced through the adsorbent. The process is therefore active rather than passive. Many experimental studies of adsorbents use a defined level of airflow, which again may not allow for simple translations to cultural heritage environments. Adsorbents incorporated into small spaces such as display cases or storage containers must also not significantly alter the relative humidity of the space. Many cultural objects require stable relative humidity. Some adsorbents readily collect water molecules and therefore may affect the humidity of a surrounding environment. As an example, silica gel is a hygroscopic adsorbent that easily attracts water. It is often conditioned to a certain relative humidity and placed inside display cases to maintain that humidity level. Dried silica gel would therefore adsorb water molecules in a given space, decreasing the humidity. Silica gel has also been shown to adsorb organic pollutant molecules in cultural heritage environments (McGath, McCarthy and Bosworth 2014). Other needs and practical considerations for adsorbent use in collections includes affordability, reusability, long-term effectiveness, long-term chemical stability, and desorption properties. Long-term chemical stability implies that the adsorbent will not degrade overtime or produce harmful emissions during use. Desorption properties require that the adsorbent will not desorb harmful pollutants during use.

Finally, some recent discussion has focused on finding or developing adsorbents that will only selectively collect gas molecules deemed harmful to collections. As an example for such a need, one study observed that zeolite Type 4A, silica gel, and activated carbon placed next to cellulose acetate collected both acetic acid and diethyl phthalate (DEP). While acetic acid is a common degradation product of cellulose acetate and can easily harm other collection materials, DEP is a product of the plasticizer used in cellulose acetate. This implies that the adsorbents may cause unwanted plasticizer loss and deterioration of cellulose acetate materials (Shashoua, Schilling and Mazurek 2014). At the time of this report, such adsorbents have not yet been developed for cultural heritage applications.

Beyond air purification, which will be the main application discussed throughout

this document, adsorbents have a number of practical uses. They can be used for drying petrochemical gases (Terrigeol 2015), chromatography and ion exchange (Snyder 1968), carbon capture and storage (Boot-Handford, et al. 2014), gas separation (Yang 1986), water purification (Singh, et al. 2018), and hydrogen storage for fuel cells (Dillon and Heben 2001), among many other applications. Additionally, new types of adsorbents with specific properties are constantly under development. Some examples include mesoporous molecular sieves, sol-gel based metal oxides, carbon molecular sieves, super-activated carbon, and carbon nanotubes (Yang 2003). It is possible that such adsorbents may find applications in cultural heritage, although they are not as widely available as more traditional, commercial adsorbents.

This report discusses general information about adsorbents, focusing primarily on the most widely used commercial materials: activated carbon, silica gel, activated alumina, zeolites, and polymer-based adsorbents. There is also a discussion of results from a study on exposing different zeolites and activated carbon to acetic acid gas. The information is intended to give an overview of adsorption processes and the capabilities of different adsorbents so cultural heritage professionals can make scientifically informed decisions for their collections. The *Background* section of the report discusses important concepts in adsorption theory such as physical adsorption (physisorption), chemical adsorption (chemisorption), adsorbent capacity, and the process of removing adsorbed compounds (desorption). This section also describes the major types of commercial adsorbents, their adsorption mechanisms, affinity for water, pore structures, and common uses. Existing heritage preservation literature is presented for each type of adsorbent discussed. *Practical adsorbent considerations* focuses on applying adsorbents in cultural heritage environments, discussing aspects that should be considered when choosing an adsorbent. Such aspects include adsorbent cost; environment humidity; target gases; and the physical form, particle size, pore size, selectivity, and capacity of the adsorbent. While it can be difficult to determine the amount of adsorbent to use and how long it will last, such points are also discussed in this section. Some suggestions are made as to how one can indicate if an adsorbent is functioning properly. *Survey of adsorbent use in Swedish cultural heritage institutions* discusses the results from a questionnaire prepared by the Swedish National Heritage Board and sent to Swedish conservators and collection managers in 2018. The answers are compiled from 182 contributors and discuss each institutions' experience with and questions concerning adsorbents. Finally, the *Zeolite and activated charcoal study* presents results from a preliminary investigation of the stated adsorbents exposed to acetic acid gas. The study is separated into three major parts: active (forced air) adsorption experiments performed at Camfil, passive adsorption experiments performed at Research Institutes of Sweden, and a case study performed at Visby Regional State Archive. The performance of three different zeolite adsorbents (type 4A, Type 5A, and Type 13X) are compared to each other and to granular activated carbon. The study provides some insight into how different zeolites function under typical cultural heritage conditions, i.e. low airflow, low pollutant concentrations, room temperature, and moderate humidity. As there is little technical information comparing different zeolites under such conditions, this study helps to elucidate such behavior.

Background

Adsorption theory

Adsorption is the process of ions, atoms, or molecules adhering to a surface. This phenomenon arises as the result of surface energy. In the bulk of a material, the bonding requirements of atoms are filled by other, surrounding atoms. On the surface of a material, some atomic bonding requirements are not filled, resulting in residual energy. Surfaces therefore have greater energy in comparison to the bulk and the excess energy attracts adsorbates. Such a process can occur between different types of interfaces, primarily liquid-solid and gas-solid interfaces. This study will focus solely on adsorption from a gas onto a solid. As mentioned in the introduction, a material with a high surface area has many available adsorption sites. Porous materials are therefore commonly used as adsorbents because they typically have very high surface areas.

Surface adhesion can be physical or chemical in nature. Physical adsorption, or physisorption, occurs as the result of weak van der Waals forces between the adsorbent and adsorbate. Chemical adsorption, or chemisorption, arises due to chemical interactions between the adsorbent and the adsorbate, resulting in stronger chemical bonds. Desorption occurs when such binding forces are overcome. This desorption process can in some cases regenerate the adsorbent, freeing up previously occupied adsorption sites that can be reused. As weak van der Waals forces require less energy to disturb than chemical bonds, adsorbents that work by physisorption are easier to desorb and regenerate. Many materials based on chemisorption phenomena cannot be regenerated as the chemical nature of the surface is permanently altered by reactions with an adsorbate.

The ability of a material to adsorb a certain substance is dependent on many factors, making adsorbent characterization and selection complex. Some factors are due to the inherent properties of the adsorbent, such as the adsorbent material, surface area, pore size, pore size distribution, density, and particle size. Interactions between adsorbent and adsorbate are also important. Other parameters that affect adsorption include temperature, humidity, airflow, and chemical makeup of the gas stream. The following sections will discuss theoretical aspects of adsorption in further detail.

Physisorption (physical adsorption)

Physisorption is an attraction between an adsorbent and adsorbate, primarily through weak van der Waals forces. It may also be the result of electrostatic forces between two oppositely charged particles. Physisorption can occur on the exterior surface of an adsorbate and on inner surfaces such as pore walls. During this process, the chemical structureof the adsorbate is not altered. Due to the weak forces between adsorbent and adsorbate, physisorption can be reversible by

applying enough energy to force desorption. Adsorbents that employ physisorption are therefore typically regenerable and can be reused. Regeneration is often performed by applying high temperatures or decreasing pressure. As the chemical structure of the adsorbate is not altered during physisorption, it will return to its original gaseous state during desorption (Rouquerol, et al. 2014).

As temperature increases in an adsorption environment, the possibility for physisorption decreases. Additionally, an increase in temperature may provide enough energy to force desorption. Adsorbents that employ physisorption should therefore not be used in high temperature applications. This is not a concern for cultural heritage environments as adsorbents are typically used under room temperature conditions. Finally, physisorption processes tend to reach equilibrium faster than chemisorption (see the section on *Chemisorption* below). This is because there is a lower energy barrier to overcome to form a weak physical interaction between adsorbent and adsorbate.

Chemisorption (chemical adsorption)

During chemisorption, an adsorbate binds with the surface of an adsorbent. The binding energies are generally equivalent to those of a chemical bond, and a chemical reaction will often result. While this reaction removes pollutants, it may also create new gases (ASHRAE Handbook 2015). In comparison to physisorption, chemisorption is much more compound specific, which may be beneficial depending on the application. Chemisorption will only occur between an adsorbate and adsorbent surface if possibility for chemical bonding exists. The surfaces of adsorbents can be chemically treated to incorporate chemisorption processes and increase specificity. For example, activated alumina can be impregnated with potassium permanganate (a strong oxidant) to add a chemisorption effect. As reactions occur, the amount of available potassium permanganate will decrease. Eventually the adsorbent will no longer work by chemisorption.

Unlike physisorption, chemisorption is not a reversible process. The bonds that form during chemisorption require more energy to dissociate, making desorption more difficult. Additonally, the chemisorbent and the adsorbate are often chemically altered during reaction. Potassium permanganate will oxidize adsorbate molecules, dissociating their bonds and forming new products. Regeneration is therefore not possible because neither the adsorbate nor the chemisorbent can be recovered in their pre-sorbed state. It may be possible to reuse the adsorbent for its physisorption properties.

Other notes about chemisorption include that it is more effective at higher temperatures and tends to reach equilibrium at a slower rate compared to physisorption. The formation of chemisorbed bonds requires more energy. Increases in temperature help to supply such energy, thus increasing the possibility for reaction. Upon further increase in temperature, the provided energy may reach a point at which chemical bonds are broken and desorption is initiated. Chemisorption media are therefore recommended for higher temperature

applications, but only up to a certain point. Such high temperature processes are not applicable to cultural heritage environments.

Desorption and regeneration

As can be gleaned from the previous sections on physisorption and chemisorption, both adsorption and desorption processes are dependent on binding energy requirements between adsorbent and adsorbate. Desorption occurs when there is sufficient energy available to overcome the weak van der Waals forces in physisorption or the stronger chemical bonds in chemisorption. Desorption depends on both temperature and the binding energy between the adsorbate and adsorbent. Once the binding forces are dissociated, the adsorbate releases from the adsorbent, freeing up surface space. While both chemisorbents and physisorbents can undergo desorption, only physisorbents are regenerable. This is because the surfaces of chemisorbents are often chemically altered during adsorption and cannot be reverted to their original state. Physisorption sites are returned to their original state and can be reused for future adsorption.

In industrial gas separation practices, adsorption and desorption occur in a cyclic manner. The desorption stage of the cycle involves either increasing the temperature using a heated gas or decreasing the pressure applied to the adsorbent (Yang 1986). Temperature increases are only used for physisorption-based materials. For adsorbents used in cultural heritage contexts, regeneration is performed using high temperatures under vacuum or an inert gas flow. It is highly recommended to send adsorbents to a laboratory or service provider for regeneration unless the appropriate laboratory tools for safe desorption are available. The desorption temperature depends on the adsorbent and the adsorbate. For example, the optimal temperature for desorbing water molecules from silica gel is approximately 150 °C, but for zeolite Type 5A the temperature must be greater than 350 °C (Basmadjian, Ha and Proulx 1975). Adsorbents can be regenerated at temperatures greater than the stated optimal temperature, but this results in extra heat expenditure without increasing desorption. Regeneration for cultural heritage adsorbents can be performed on a determined schedule (e.g. once a year). It can also be performed when the adsorbent is no longer efficiently adsorbing pollutants. Practically speaking, regeneration will not remove all adsorbates. After regeneration, activated carbon was found to have about 50% of its original capacity to adsorb volatile organic compounds (U. S. Environmental Protection Agency 1999). This may be due to difficulties in removing adsorbents from the smallest pores.

In some cases, desorption can occur at typical ambient conditions, like inside museum display cases. It is possible for strongly sorbing compounds to displace weakly sorbing compounds, forcing the latter to desorb. As an example, toluene has been found to displace isobutanol from its adsorption site on activated carbon, causing it to desorb (VanOsdell et al. 1996). This can be a concern if the displaced compound is of concern for the particular application. Desorption can also occur if the pollutant concentration around an adsorbent drops (Library of Congress 2012, Druzik, et al. 2003).

Capacity and isotherms

The capacity of an adsorbent is the amount of adsorbate collected per unit mass of the adsorbent under certain conditions. Those conditions include temperature and partial pressure (or concentration in the case of liquids). Partial pressure is the pressure of a single gas constituent in a mixture of gases. When an adsorbent comes in contact with a gas under constant environmental conditions, the gas molecules will adsorb until equilibrium is reached between the adsorbent and adsorbate. At this point, the adsorbent is saturated. The amount of a particular adsorbate collected under such conditions is known as the equilibrium capacity. Equilibrium capacity depends on the interactions between adsorbent and adsorbate and can be influenced by other gases in a gas mixture. For volatile organic compounds (VOCs), the equilibrium capacity tends to be larger for less volatile, higher molecular weight VOCs (Fisk 2007).

Isotherms are the primary scientific basis for adsorbent choice. They are graphical representations of an adsorbent's equilibrium capacity as a function of the adsorbate's partial pressure. For each isotherm, the temperature remains constant. An isotherm is created for each adsorbent, each individual adsorbate, and every temperature used for a particular application. It is also possible to create mixed-gas isotherms to observe the effects of multiple gases. The y-axis of an isotherm is represented by the equilibrium capacity of an adsorbent exposed to a particular adsorbate, i.e. the amount adsorbed. The x-axis is represented by the partial pressure of the adsorbate. The pressure range in an isotherm must represent the pressures used in the actual adsorbent application. Using data provided by isotherms, one can determine which adsorbent has the greatest equilibrium capacity for a particular adsorbate.

Isotherms can be determined experimentally using a variety of techniques, including gas manometry, gas adsorption gravimetry, and gas adsorption calorimetry. One study by Cruz, et al. developed an isotherm for nine different adsorbents (activated charcoals, zeolites, silica gel) exposed to low pressures of acetic acid at 25 °C. The measurements were performed with museum atmospheres in mind. For the majority of tests, the highest pressure of acetic acid gas was approximately 0.04 kPa, which corresponds to an atmospheric concentration of 400 parts per million (ppm) or 1 g/m^3. In comparison, acetic acid concentrations of 1 ppm is considered high for cultural heritage collections (Grzywacz 2006). Isotherms determined for low concentrations can be practically difficult due to the length of time required to reach equilibrium. According to the obtained data, zeolite NaX and an extruded activated carbon adsorbed the most acetic acid (Cruz, et al. 2004).

There are a number of mathematical models and equations developed to interpret and predict isotherm behavior. A discussion of such models is beyond the scope of this report, but can be obtained from many other sources (Yang 1986, Basmadjian 1997, Rouquerol, et al. 2014, Tien 2019, Sing, et al. 1985). Such equations can be used to predict the amount of a particular gas that will adsorb onto an adsorbent using known quantities (e.g. temperature and pressure) and data from a limited

number of experiments. Desorption isotherms for an adsorbent can also be measured or calculated. Developing an appropriate adsorption-desorption isotherm for a particular application helps to characterize the adsorbent and determine if the adsorption process is favorable or unfavorable. Certain isotherm shapes can help to infer the pore sizes found in an adsorbent (Tien 2019, Brunauer, et al. 1940). An adsorbent that exhibits favorable behavior has an isotherm that is convex in shape, indicating that there is a large amount of adsorption at low partial pressures. An unfavorable isotherm has a concave shape, indicating that significant adsorption only occurs at high partial pressure.

Common types of adsorbents

The most common adsorbents are activated carbon, activated alumina (Al_2O_3), silica gel (SiO_2), zeolites, and polymeric adsorbents. Some of these materials, like activated carbon and some zeolites, are created from existing, naturally made materials. Others are synthetically manufactured. The following section will discuss each of the five adsorbent categories in more detail. Activated carbon is known for being a general adsorbent and is used to adsorb a wide variety of compounds. Activated alumina can be easily tailored for specific applications by modifying its surface. Silica gel is often used to control humidity due to its affinity for water adsorption. Zeolites have very uniform pores and are employed for their ability to adsorb molecules based on their size. Polymeric adsorbents covers a range of cross-linked resins that can be tailored for specific applications.

Table I: Collected data on physical properties of common adsorbents. Data is from Basmadjian 1997, Tien 2019, and Yang 1986.

Adsorbent	Particle diameter (mm)	Density (kg/m^3)	Pore diameter (Å)	Surface area (m^2/g)	Porosity
Activated carbon	1–5	500–900	10–25	300–4000	0.4–0.7
Activated alumina	2–12	650–1000	10–80	250–350	0.5–0.77
Silica gel	1–7	700–1000	10–400	300–850	0.4–0.7
Zeolites	1–5	1100	2–10	200–600	0.2–0.5

Many physical properties of adsorbents affect their performance and affinity for certain adsorbates. Such properties include surface area, pore diameter, pore size distribution, density, and diameter of the adsorbent particle. The temperature, humidity, and air pressure of the surrounding environment, as well as the bonding characteristics between the adsorbent and adsorbate will also affect adsorption (Parmar and Grosjean 1991). Table I provides collected information on the physical properties of common adsorbent classes (Basmadjian 1997, Tien 2019, Yang 1986).

Adsorbent particle diameter can affect the rate of adsorbate uptake. Smaller particles tend to adsorb at a faster rate than larger particles by increasing mass transfer of the adsorbate. In situations where air is forced through an adsorbent (e.g. HVAC filtration), the particle size affects pressure drop, which is the change in pressure of an air stream as it passes through an adsorbent layer. Smaller particles create larger pressure drops, which can increase energy expenses (Fisk 2007). For many active adsorption processes, pressure drop should ideally be low and particles should have sufficiently large diameters to reduce change in pressure (Muller 2011). In some situations, other factors may take precedence. For example, during single pass filtration (outdoor air filtration), pollution adsorption efficiency is important, which means that small particles are necessary. During multi-pass filtration (indoor air recirculation), lower pollution adsorption efficiency is acceptable. In such cases, large adsorbent particles can be used, which also results in reduction of pressure drop and energy.

The porosity gives an idea of how much of the adsorbent is composed of voids and pores. The numerical value for porosity represents the total pore and void space divided by the total volume of the adsorbent. A value closer to 1 indicates a higher porosity. The specific surface area of an adsorbent is its surface area per unit mass. As adsorption is a surface phenomenon, a high surface area is generally beneficial as it indicates that there are more available adsorption sites. Surface area therefore affects the capacity of an adsorbent, and to a lesser extent, the adsorbate uptake rate (Tien 2019).

Pore size in adsorbents is often simplified to refer to the diameter of a cylindrical pore or the available distance between two opposite walls (Rouquerol, et al. 2014). For pores that have irregular shapes, the smallest dimension within a given pore is the point that defines pore size. Pore sizes are divided into three major categories, as recognized by the International Union of Pure and Applied Chemistry (IUPAC) (Sing, et al. 1985):

Macropores: have internal widths greater than 50 nanometers (500 Å)

Mesopores: have widths between 2 and 50 nanometers (20 and 500 Å)

Micropores: have internal widths less than 2 nanometers (20 Å)

Each type of pore physisorbs in a particular way. Macropores are large enough to be considered single, flat surfaces as adjacent or opposite walls within the pore do not affect the adsorption process. Mesopores can exhibit capillary condensation, which is when an adsorbate condenses from a gas to a liquid phase. This occurs when adsorbed molecules on opposite walls become close enough to attract each other, condensing into a liquid. Capillary condensation affects desorption as the condensed molecules will not desorb simply by a reduction in pressure. Other driving forces may be required to remove the molecules. Micropores are similar in diameter to the adsorbate molecules. Van der Waals forces from the opposite and adjacent walls of the pore therefore affect the adsorption process in micropores.

Many adsorbents have a range of pores sizes and pore shapes, referred to as the pore size distribution. Activated carbon, activated alumina, and silica gel all have a wide distribution of pore sizes. Conversely, zeolites have very defined, singular pore sizes and very narrow distributions. Polymeric adsorbents can be synthesized to have either defined pore sizes or a wide distribution. The available pore size distribution in a particular adsorbent can be measured using techniques such as mercury porosity, nitrogen adsorption and desorption, and molecular sieving (Tien 2019). As many of the common adsorbents have a range of pore sizes, this creates a highly complex network of pores that can often be difficult to define and characterize.

Adsorbents are manufactured and sold in a variety of shapes and sizes, and are incorporated into various media. Most typically, they are sold as cylindrical pellets, granules, powders, and spheres. There has also been a rising interest in structural adsorbents such as monoliths, foams, and laminates. Monoliths, for example, are structures composed of identical, parallel channels and are used for active applications to reduce pressure drop (Rezaei and Webley 2010). Adsorbents can be embedded into fabrics and mixed into paints. Activated carbon fabrics were first used in the 1980's for air purifiers (Bailey and Maggs 1980). Carbon cloths are commonly used in cultural heritage applications to line storage containers or display cases.

In addition to the common adsorbents mentioned, newer adsorbents such as metal organic framework (MOFs) and covalent organic frameworks (COFs) are under investigation. Both materials are porous crystalline solids. MOFs are made by linking inorganic and organic units using strong bonds. They are highly flexible in terms of their geometry, size, and functionality. There are reportedly over 20,000 different types of MOFs (Furukawa, et al. 2013). COFs are organic units built with strong covalent bonds and are highly crystalline materials. They have a high surface area (greater than 1500 m^2/g), high thermal stability, and pore sizes ranging from 7 to 27 Å (Cote, et al. 2005). Such materials have the potential for a range of applications, including gas storage, gas adsorption, catalysis, and sensors (Tien 2019).

Table II below contains a summary of the information presented in the following sections. It highlights important aspects concerning the main adsorbents discussed in this document: activated carbon, silica gel, activated alumina, zeolites, and polymer-based adsorbents.

Table II: Major points about the adsorbents discussed in this document.

Adsorbent	Major notes
Activated carbon	• Made from wood, peat, coconut shell, fruit pits, coal. • Nonpolar, lower affinity for water. • Tends to adsorb more nonpolar or weakly polar compounds. • 'General adsorbent' often used for air and water filtration. • Wide pore size distribution, contains many micro- and mesopores. • Physisorbent unless chemically impregnated. • Relatively easy to desorb/regenerate.
Silica gel	• Made from silica, SiO_2. • Amorphous. • Polar, strong affinity for water. • Easily desorbs water. • Commonly used as a desiccant or humidity buffer. • Wide pore size distribution, primarily mesoporous. • Physisorbent.
Activated alumina	• Crystalline. • Polar, strong affinity for water. • Commonly used as a desiccant. • Wide pore size distribution, contains many meso- and macropores. • Easily modified through surface treatments, often sold as a chemisorbent.
Zeolites	• Crystalline aluminosilicates. • Approximately different 200 zeolites in existence. • Uniform, ordered pores on the micropore scale ('molecular sieves'). • Often used to filter molecules based on size. • Produced naturally and synthetically. • Mostly polar, used to create very dry atmospheres.
Polymer-based adsorbents	• Composed of rigid, crosslinked polymer networks. • Can be polar or nonpolar. • Used in gas chromatography columns, water treatment, VOC collection. • Some known to desorb at low temperatures.

Activated carbon

Activated carbon is one of the most widely used adsorbents due to its versatility, availability, and affordability. Its manufacture dates back to the 19th century and its commercial uses greatly expanded during World War I when it was used to filter toxic gas. Activated carbon primarily works by physisorption but can be

impregnated with certain compounds to create a chemisorbent material. It is commonly used because of its high available surface area, large volume of micro- and mesopores, and relatively easy regenerability. It is nonpolar and therefore has a lower affinity for water adsorption compared to other common adsorbents. Physical forms of activated carbon include granules, pellets, powders, textiles, and foams. It is commonly used to adsorb organic compounds, nonpolar molecules, and some weakly polar molecules. Common applications include wastewater treatment, industrial gas treatment, and air purification. Activated carbon is amorphous and contains a highly complex network of pores and voids, often making it difficult to characterize. New carbon-based materials, such as carbon molecular sieves, have more well defined pore structures and allow different molecules to diffuse at different rates based on their diameters. Carbon molecular sieves are primarily used to separate nitrogen from air and are typically not used for air purification.

Production of activated carbon involves pelletization, carbonization, and activation. It is often made from wood, peat, coal, coconut shell, and fruit pits. Major coal sources used include anthracite and bitumous coals (Yang 1986). Although there are many types of carbon available, it can be difficult to predict which type is best for a specific application. During production, carbonization involves drying and heating the pelletized source material to remove gases and byproducts such as tar. The material must be heated to temperatures greater than 400 °C with inert gases such as argon and nitrogen to create an oxygen-free atmosphere. Activation involves exposing carbon to an oxidizing agent, such as steam or carbon dioxide, at temperatures above 250 °C. This creates the porosity and high surface area by burning off pore-blocking structures, such as carbon residue, that are created during the carbonization step (Yang 2003). During this process, carbon can be impregnated with chemicals before carbonization to tailor its adsorption properties. Such chemicals include acids (e.g. phosphoric acid), strong bases (e.g. potassium hydroxide, sodium hydroxide), or salts (e.g. potassium iodide, calcium chloride). Carbon impregnated with strong bases have an affinity for adsorbing acidic gases such as sulfur dioxide, acetic acid, and formic acid. Carbon impregnated with potassium iodide and iron oxide is used to remove hydrogen sulfide gas. As a note, activated carbon impregnated with iron oxide can produce elemental sulfur, possibly creating sulfuric acid that can react with cultural heritage. Potassium iodine-impregnated carbon does not suffer from this issue (Grzywacz 2006). Impregnated activated carbon products work by chemisorption. They will lose their chemisorption properties during the regeneration process but will continue to work by physisorption after regeneration.

As can be seen from Table I, activated carbon has a high surface area due to its large amount of micropores and mesopores. Materials with different pore sizes can be used for different applications. Activated carbon containing a large number of micropores (between 10 and 25 Å) is better for gas applications. Activated carbon containing a large number of mesopores (close to or greater than 30 Å) is better for liquid applications due to the larger size of many adsorbates in the liquid phase (Yang 2003). In the gas phase, non-impregnated carbon is known for removing chlorine, nitrogen dioxide, organic acids, and volatile organic compounds (VOCs)

(Grzywacz 2006). Compared to other commercial adsorbents, activated carbon tends to adsorb more nonpolar or weakly polar organic molecules. Additionally, regeneration is often easier than with other adsorbents. This is due to the weak forces that adhere the adsorbate to the carbon surface during physisorption. Less energy and therefore a lower temperature is required to overcome these forces and initiate desorption.

The surface of activated carbon is primarily nonpolar but may be slightly polar due to the presence of surface oxides or inorganic impurities, making it unique among common adsorbents (Yang 1986). In comparison, silica gel, activated alumina, most zeolites, and some polymeric adsorbents are polar materials, giving them a higher affinity for water adsorption (Basmadjian 1997). Due to its nonpolar nature, activated carbon has a lower affinity for moisture, but should not be considered hydrophobic as it can still adsorb some water. At high humidity, water does compete for sites with other compounds on activated carbon, possibly causing the other compounds to desorb or not adsorb at all (Werner 1985, Nelson, Correia and Harder 1976). At low and moderate humidity, organic, nonpolar, and weakly polar compounds will adsorb more preferentially onto activated carbon than water. Desired adsorbates will therefore not compete as much with water molecules for adsorption sites. Of the major adsorbents, activated carbon is the only material that does not require intensive moisture removal before use. It is therefore not commonly used as a desiccant but is more desirable for water filtration applications or processes requiring humidified atmospheres.

In cultural heritage contexts, activated carbon is commonly used due to its simplicity, affordability, and the wide range of adsorbates. It is often used in a granular or pelletized form inside breathable sachets or trays that are placed in hidden drawers beneath a display case. Activated carbon in textile form is also useful for lining storage containers or display cases. Despite its practicality, carbon textiles are known to require more frequent replacement than granular carbon, cannot be regenerated, and can produce carbon dust. Additionally, some textile materials contain chlorine compounds that may affect cultural heritage objects (Rimmer, et al. 2013). Activated carbon can also be incorporated into foam materials. A study by Grøntoft et al. observed differences in deposition velocities of formic and acetic acid on activated charcoal cloth, foam, and granules inside display cases. It was found that the carbon cloth had the highest deposition velocity of pollutants, followed by the foam, and finally the granules. This may have been due to a smaller particle size and pore size of the carbon granules incorporated into the cloth and foam (Grontoft, Lankester and Thickett 2015).

Several studies investigated the performance of activated carbon materials in cultural heritage environments and compared them to other common adsorbents, including zeolites, clays, activated alumina, and silica gel (Brokerhof 1998, Cruz, et al. 2004, Cruz, et al. 2008, Dahlin, et al. 2013, Ecob, et al. 2014, Parmar and Grosjean 1991). Gases investigated include acetic acid, formic acid, formaldehyde, SO_2, O_3, NO_2, and toluene. All studies noted that activated carbon materials were able to maintain the lowest pollutant concentrations, even during long-term studies

over several months. Some adsorbents, such as zeolite Type 13X and polymer adsorbent Chromosorb performed as well as carbon, but are more expensive and not as readily attainable as activated carbon. Conversely, because activated carbon is known to adsorb a wide range of molecules, it does not have the same selectivity as other adsorbents and therefore may adsorb volatiles that do not require removal.

Silica gel

Silica gel is composed of amorphous, chemically inert silica, SiO_2. It is a rigid network of spherical silica particles that can take on a number of properties or pore structures depending on the production process. Silica gel is known for its large water capacity and is commonly used as a desiccant. In cultural heritage applications, silica gel is used to maintain stable relative humidity levels inside enclosed spaces such as display cases. While it has a strong affinity for water, silica gel adsorbs other volatile compounds that are more difficult to remove during regeneration (McGath, McCarthy and Bosworth 2014). In research and industrial applications, silica gel is used for chromatography, drying air, adsorbing heavy polar hydrocarbons from natural gas, and removing toxic substances from air. There are two main kinds of silica gel, both of which are mesoporous. Regular density silica gel has a surface area between 750 and 850 m^2/g and an average pore diameter of 22 to 26 Å. Low density silica gel has a surface area between 300 and 350 m^2/g and an average pore diameter of 100 to 150 Å.

The fabrication of silica gel involves reacting an aqueous solution of sodium silicate with an acid such as acetic acid, hydrochloric acid, or sulfuric acid. This produces finely divided particles of hydrated SiO_2 which polymerizes into a gelatinous precipitate, silica gel. The resulting material is washed, dried, and activated. After-treatments, such as aging or pickling, can also be performed to initiate certain surface properties. The silica gel end product can have a range of different pore structures and pore size distributions. These properties are dependent on processing parameters like temperature, pH, silica concentration, and the after-treatments. Silica gel is often sold as spheres or in a powder form, and is colorless unless a color indicator is added. Color indicators include ammonium tetrachlorocobaltate or cobalt chloride. They appear pink when hydrated and blue when dry.

As it is primarily used as a desiccant, silica gel is well known for its large capacity to hold moisture. This is because it is a polar material and therefore has an affinity for attracting water molecules. Like activated alumina (discussed in the next section), silica gel will uptake the greatest amount of water at moderate and high humidity. It is therefore often used to reduce humidity in very humid air (Basmadjian 1997). Silica gel is also relatively easy to regenerate due to weak physisorption forces between water and the adsorbent surface. Many zeolites must be heated to temperatures exceeding 350 °C to remove water, while silica gel only requires heating to 150 °C (Breck 1974). Silica gel can adsorb compounds other than water that may not fully desorb at 150 °C. For cultural heritage applications, it is suggested to heat silica gel to 200 °C to remove moisture if it does not contain

indicator dyes, and to 120 °C if it does contain indicator dyes (Weintraub 2002). Despite such recommendations, it has been found that silica gel still contains compounds such as acetic acid, formic acid, and hydrochloric acid after heating at 200 °C for several days (McGath, McCarthy and Bosworth 2014). If silica gel is being used for humidity control in cultural heritage environments, one must be aware that higher temperatures may be required for regeneration to remove all adsorbates. It is possible that adsorbates other than water could desorb over a long period of time or when the silica gel is exposed to new display or storage environments.

While silica gel is traditionally used for moisture adsorption, there are recent investigations into developing silica materials specifically for scavenging air pollutants. Such materials are different from commercial silica, as they have ordered, uniform pore structures that are controlled by altering the pH during processing (Brinker and Sherer 1990). One particular silica material, known as MCM-41, has been used for VOC and sulfur dioxide removal (Izumi 1996, Teraoka, et al. 2000, Zhao, Ma and Lu 1998). It has a large, uniform pore structure and large pore volume. Desorption was performed easily due to weak bonds formed with the adsorbent surface. MCM-48 has also been used to adsorb CO_2 and H_2S, and can be regenerated at low temperatures of 60 °C (Huang, et al. 2003). Some studies suggest that while MCM-41 can adsorb a large amount of compounds in comparison to other common VOC adsorbents, it does demonstrate a decrease in VOC adsorption at high relative humidity (Idris, et al. 2010).

Activated alumina

Similar to silica gel, activated alumina (Al_2O_3) is used as a desiccant due to its high capacity for water and easy regenerability. While silica gel is an amorphous material, activated alumina is typically crystalline. It is also known for its versatility as the surface and pore characteristics are easily modified through treatments using acids, alkaline solutions, or thermal processes. It is often used for drying air streams and chromatography, and is also incorporated into some HVAC air filters for pollutant filtration.

Activated alumina is polar, which contributes to its high uptake of moisture. Like silica gel, it adsorbs water at moderate and high relative humidity and is often used to reduce moisture in very humid air streams (Basmadjian 1997). The production of activated alumina involves dehydrating and heating aluminum hydrates (e.g. aluminum trihydtate or gibbsite) in air to temperatures above 400 °C. The resulting product has many pores with diameters greater than 50 Å. As activated alumina is versatile, it can be tailored for different applications. For example, alumina containing high soda content is often used to remove acid gases such as carbonyl sulfide (COS), carbon dioxide (CO_2), or hydrogen sulfide (H_2S). Activated alumina impregnated with alkaline compounds like potassium oxide (K_2O) or sodium oxide (Na_2O) are used for removing sulfur gases, carbon dioxide, and nitrogen oxides (Yang 2003). For HVAC pollutant filtration applications, activated alumina is often impregnated with potassium permanganate ($KMnO_4$), a strong oxidant, to remove

nitrous oxide (NO), aldehydes, sulfur oxides, amines, and organic acids (Grzywacz 2006). A study by Camfil investigated $KMnO_4$-impregnated alumina compared to activated carbon for use in filtered HVAC systems. The study used low concentrations of NO_2, SO_2, O_3 and toluene over the course of many hours and found that the impregnated alumina was not as effective as activated carbon in removing the four pollutants (Ecob, et al. 2014). It is possible that activated alumina impregnated with potassium permanganate is useful for other important pollutants in museum environments such as formaldehyde.

Treated activated alumina works via chemisorption and therefore cannot be regenerated without losing its chemisorption properties. Potassium permanganate gives activated alumina media a bright pink appearance that will turn brown when the chemisorbent is exhausted. While this color change provides indicates when the media requires replacement, it is not renegerable and is a toxic substance that must be disposed of as hazardous waste.

Zeolites

Zeolites are crystalline aluminosilicate adsorbents that have very small, regular pores. Unlike the previous adsorbents discussed, which all have a range of pore sizes, zeolites have uniform pore sizes. For example, zeolite 4A has well-ordered pores all with an effective aperture of 3.8 Å in diameter. Due to this property, zeolites are often used for their ability to separate adsorbate molecules based on their size. Zeolites will adsorb molecules that are small enough to fit inside their pores. Zeolites are therefore part of a class of material known as molecular sieves. While all molecular sieves filter molecules based on size, only zeolites are composed of crystalline aluminosilicates. Other types of molecular sieves are based on carbon, silica, and clays, and will not be further discussed in this document. Zeolites are created naturally or synthetically. Approximately 200 different types have been found or synthesized. The first natural zeolites were discovered in 1756 by Axel Fredrik Cronstedt and the first synthetic zeolite was created in 1862 by H. Saint-Claire Deville. By the mid twentieth century, Union Carbide initiated the commercial production and sale of synthetic zeolites (Milton 1959, Milton 1989). Due to their size exclusion capabilities, zeolites are popular for filtering hydrocarbon mixtures, converting crude oil to petroleum products (catalytic cracking), air separation, and chromatography. Most zeolites are polar and adsorb moisture. They are used as desiccants and for drying air streams. Like the previously discussed physisorbents, zeolites can be regenerated by heating, but often require temperatures greater than 300 °C (Yang 2003).

Natural zeolites are crystals that are altered through interactions with saline water. They are often found in lake sediments, marine sediments, metamorphic rock, and volcanic tuff (Jha and Singh 2016). Natural zeolites are not as extensively used as synthetic zeolites, but are easily available and often more affordable (Ackley, Rege and Saxena 2003). There are over 40 different types of natural zeolites, including chabazite, gmelinite, mordenite, clinoptilolite, and faujasite. The most common synthetic zeolites are manufactured starting with raw materials containing silica,

alumina, and alkali metal hydroxides. A gel is formed at room temperature using sodium hydroxide, sodium silicate, and sodium aluminate in an aqueous solution. The gels are then crystallized at temperatures up to 300 °C, followed by an ion exchange process using cations such as Na^+, Li^+, Ca^{2+}, K^+, and NH_4^+. The crystals are dried and often formed into pellets with or without a binder. Synthetic zeolites are typically identified by three letter structure codes. Some examples include LTA for Linde Type A, FAU for faujasite, and ZSM for zeolite socony mobil. The International Zeolite Association website has a database of different zeolite types, including drawings and their three letter structure codes (International Zeolite Association n.d.).

The stoichiometry of a zeolite is $M_{x/n}[(AlO_2)_x(SiO_2)_y]zH_2O$, where x and y are integers ($y/x \geq 1$), n is the valence of a cation M, and z is the number of water molecules in each unit cell (Yang 1986). The water molecules can be removed with heat and evacuation. The primary crystalline units of a zeolite are the tetrahedra of silicon and aluminum, SiO_4 and AlO_4. These primary units assemble into secondary units such as cubes, octohedra, hexagonal prisms, and truncated octohedra. The secondary units assemble to form a three dimensional crystalline network containing windows and cavities (i.e. pores). Varieties of zeolites exist because the tetrahedra units can be arranged in a number of different ways. The aluminum tetrahedra give the zeolite framework a negative charge, which is balanced by incorporating positively charged cations (M). The cations are ion exchangeable. This property is often utilized in waste water treatment in which cations within the zeolite structure (Na^+, for example) are exchanged with cations in the waste water (e.g. NH_4^+) (Jha and Singh 2011). Different cations in zeolites provide the microstructure with different window aperture diameters (Payra and Dutta 2003). The diameter of the window determines the size exclusion properties of a zeolite. Adsorbate molecules smaller than the window diameter will be allowed into the crystal cavity for adsorption, while molecules larger than the window diameter will not pass and will not be allowed into the crystal cavity. The size of this window aperture can be controlled during synthesis.

The most common zeolites are Type A, Type X, and Type Y. Their primary units are composed of a truncated octahedron, also called a sodalite cage. This primary unit is shown in Figure 1a and is used to assemble the unit cells of zeolites Type A (seen in Figure 1b), Type X, and Type Y (both seen in Figure 1c). Type A is also known as Linde Type A (LTA), and types X and Y are also known as faujasite (FAU).

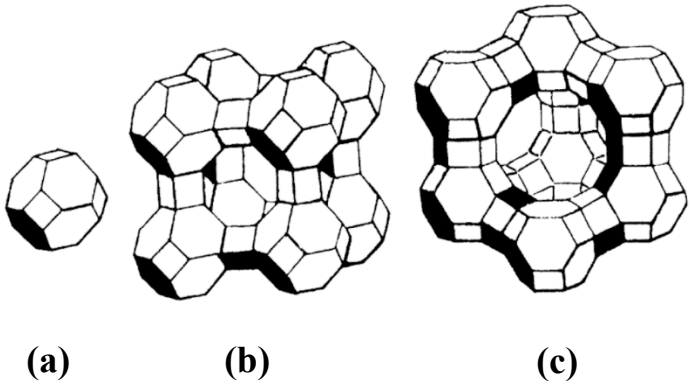

Figure 1: (a) Primary unit of zeolite types A, X, and Y, known as a truncated octahedron or sodalite cage; (b) unit cell of zeolite type A; and (c) unit cell of zeolite types X and Y (Yang 1986).

There are three forms of Type A zeolite: Type 3A, Type 4A, and Type 5A, each having their own distinct window aperture diameter. Table III includes basic information on each of the three forms. The basic unit cell of Type A contains 12 AlO_4 and 12 SiO_4 tetrahedra. Type 4A is synthesized to contain 12 sodium cations in the unit cell, creating an effective window aperture diameter of 3.8 Å. It contains sodium cations, but by exchanging Na^+ with K^+, zeolite Type 3A is created. It has a smaller effective aperture diameter of 3.0 Å due to the larger size of the potassium cations. Exchanging sodium cations with Ca^{+2} or Mg^{+2} increases the effective aperture diameter to 4.3 Å, creating Type 5A. During this process, two sodium ions are replaced by a single calcium or magnesium ion (Breck 1974). Reducing the number of cations in the structure frees up previously blocked cavity space, increasing window aperture size and altering the adsorption capabilities (Lobo 2003).

Both Type X and Type Y contain 192 tetrahedra. The specific number of silicon tetrahedra and aluminum tetrahedra per unit cell varies depending on the zeolite. The difference between Type X and Type Y is based on the number of aluminum ions per unit cell. For Type Y, the number ranges from 48 to 76, with a silicon to aluminum ratio of 1.5 to 3. For Type X, the number varies from 77 to 96, with a silicon to aluminum ratio of 1 to 1.5. The unit cell for zeolites X and Y are shown in Figure 1c. Two widely used synthetic faujasite zeolites are Type 10X and Type 13X. Calcium is the major cation for Type 10X and the structure allows molecules with effective diameters smaller than 8 Å to pass through the window aperture. Sodium is the major cation for Type 13X, and the structure can allow molecules with an effective diameter smaller than 10 Å (Breck 1974, Collins 1968).

Table III: Common synthetic commercial zeolite types and the molecule sizes they permit or exclude through their window apertures (Collins 1968).

Zeolite	Molecules adsorbed	Molecules excluded
Type 3A	Effective diameter < 3 Å	Effective diameter > 3 Å
Type 4A	Effective diameter < 4 Å	Effective diameter > 4 Å
Type 5A	Effective diameter < 5 Å	Effective diameter > 5 Å
Type 10X	Effective diameter < 8 Å	Effective diameter > 8 Å
Type 13X	Effective diameter < 10 Å	Effective diameter > 10 Å

Much like silica gel and activated alumina, many zeolites are polar and therefore easily attract water. Zeolites are known to be particularly effective at adsorbing water in low humidity. They are often used for "deep drying" of air streams if very low humidity is required for a particular application. At moderate and high relative humidity levels, silica gel and activated alumina are more effective at adsorbing water than polar zeolites (Basmadjian 1997). Water should be removed from zeolites before use. Non-polar zeolites can also be produced by using aluminum-free silica sources. Adsorption properties of zeolites depend on factors other than molecular size. In many industrial applications, zeolites are not used for their molecular sieving capabilities, but rather for their affinities for particular molecules. For example, nitrogen is preferentially adsorbed on to zeolite Type 5A over oxygen due to its strong bond with the polar surface (Yang 1986).

In cultural heritage contexts, molecular sieves are often used to adsorb acetic acid emissions from cellulose acetate film (Eastman Kodak Company n.d., Hendriks 1997). The Image Permanence Institute studied the effects of adding zeolites to microclimates containing cellulose acetate film. They found that zeolite-containing microclimates were able to maintain a steady level of film acidity compared to microclimates not containing zeolites, which showed an increase in film acidity over time (Bigourdan and Reilly 2000). The zeolites simultaneously remove water and acetic acid, reducing the rate of hydrolysis of the acetate molecules and removing the possibility for autocatylitic degradation by acetic acid (Ligterink 2002). A study by Shashoua, et al. also observed the uptake of acetic acid from degrading cellulose acetate by zeolite Type 4A (alongside other adsorbents). It was found that while the adsorbents collected both water and acetic acid, they also collected volatile diethyl phthalate (DEP), a plasticizer used in cellulose acetate film (Shashoua, Schilling and Mazurek 2014).

Zeolites have also been incorporated into archival materials such as mat board and paper (Hollinger Jr. 1997). Some studies have demonstrated the effectiveness of such products under high pollutant exposure over short periods of time (Rempel 1996, Hollinger, Jr. 1994). One investigation by the Library of Congress studied zeolite-loaded archival materials exposed to low concentrations (7 – 20 ppm) of

acetic acid under passive headspace conditions. Preliminary results indicated that zeolite-loaded materials adsorbed acetic acid faster than regular archival mat boards (Library of Congress 2012). Long-term case studies of the products have also been performed. One investigation found that zeolite-based mat boards did not have an advantage over regular archival mat board in low airflow conditions (Schaeffer, Druzik and Norton 2004). Desorption experiments showed that zeolite products released acetic acid when the environment was changed from high acetic acid concentrations to lower acetic acid concentrations, but desorbed less in comparison to non-zeolite based archival products (Library of Congress 2012, Brokerhof 1998).

Studies have compared zeolite adsorption properties to other common adsorbents such as activated carbon and silica gel. Cruz, et al. found Type 13X zeolite to have similar adsorption capacity as activated carbon RB4 when exposed to acetic acid gas under laboratory conditions, some of which simulated a passive museum display case (Cruz 2004, Cruz 2008). Researchers that were part of the MEMORI project found zeolites (unspecified) and activated carbon materials to have similar passive and active adsorption properties against acetic acid, formic acid, and formaldehyde, toluene, and alpha-pinene (Dahlin, et al. 2013). Performing long term analysis under static conditions, Brokerhof found that activated carbon products removed more acetic acid gas than zeolite Type 4A over the course of 8 months (Brokerhof 1998). Finally, Parmar and Grosjean studied the active removal of H_2S, O_3, and NO_2 in a test display case and found zeolite Type 13X to effectively remove H_2S but not O_3 or NO_2 (Parmar and Grosjean 1991).

Polymer-based adsorbents

Polymer-based adsorbents are highly tailorable materials that can be produced with a range of properties. They are typically sold in the form of spherical beads and are composed of polar or nonpolar groups in a rigid, cross-linked polymer network. This network provides the materials with the high surface area needed to perform well as adsorbents. They are often used for gas chromatography columns, water treatment, and VOC collection. As they are often very specific and more expensive than other common adsorbents, their use in cultural heritage applications is currently limited.

Polymeric adsorbents can be polar or nonpolar, and can be hydrophobic or not, depending on the synthesis process. For example, adsorbent XAD-2 is created by polymerizing styrene and divinyl benzene. Its surface contains benzene rings, and as an unfunctionalized material it is hydrophobic. Many ion-exchange polymeric resins are also synthesized by polymerizing styrene and divinyl benzene but are not hydrophobic (Yang 2003). The class of polymeric adsorbents contains some of the most hydrophobic adsorbents, providing them with advantages over activated carbon for removing contaminants from humid air. Additionally, polymeric adsorbents are generally easier to regenerate in gas phase than other adsorbents, as they are known to desorb compounds at lower temperatures (Flanagan, et al. 1994).

Practical adsorbent considerations

Adsorbent choice

Selecting an adsorbent depends on a number of factors. For cultural heritage environments, some of those factors include:

- Cost
- Humidity
- Physical form and particle size
- Target gases
- Pore size and selectivity
- Capacity
- Regenerability

Cost is often an important consideration for cultural heritage institutions. Luckily, many common adsorbent materials are affordable and reusable. Adsorbents that have not been treated for chemisorption often cost less than those that have, particularly when considering long-term use as chemisorbents can not be regenerated. Adsorbents that are sold in granular, pelletized, or powder form are also typically more affordable than those sold in the form of textiles or foams. Similar to chemisorbent materials, textiles and foams cannot be regenerated. Adsorbents that are highly selective and tailored for a specific application (e.g. many polymeric adsorbents) cost more than those that work as general adsorbents (e.g. activated carbon).

As has been discussed throughout this document, different adsorbents react to airborne moisture in different ways. Silica gel is often used to maintain stable humidity levels in display cases, but incorporating other adsorbents may affect moisture levels. Activated carbon is the only widely available nonpolar adsorbent and is less likely to affect moderate or low humidity conditions. Silica gel and activated alumina are known to adsorb moisture at moderate and high humidity levels, while zeolites are most effective at adsorbing water under low humidity conditions. If needed, adsorbents can be preconditioned to a particular humidity level before they are installed, but this can limit their capacity for other adsorbates. If humidity levels are important in a particular storage or display setting, it is recommended to monitor the space after adsorbents are installed. Humidity is also important for the adsorbent performance. Water molecules can occupy adsorption sites or displace adsorbed species in hygroscopic adsorbents like zeolites, silica gel, and activated alumina, reducing their capacity for other molecules. While nonpolar, activated carbon can be affected by moisture as well, but this usually occurs at high humidity levels.

Adsorbents are sold in many available physical forms and particle sizes. Smaller particle sizes generally adsorb at a faster rate than larger sizes, although this may not be a concern for long-term, passive adsorption environments. Particle size is primarily a concern for active filtration due to its effect on pressure drop (discussed

under *Common types of adsorbents*). Particle size and physical form may affect handling and placement in cultural heritage environments, as it is often easier to handle fabrics and foams than loose granular or powdered material. Some adsorbents can produce dust, even in the form of a fabric or foam. This must be taken into consideration before using any adsorbents in close proximity of an object.

Target gases are often difficult to define in cultural heritage environments. The atmospheres in display cases, galleries, and storage spaces are often complex mixtures, dependent on materials in the collection or on materials used to house objects. Additionally, many cultural heritage institutions do not have the finances or resources to perform regular air quality analysis. The most important pollutants to consider are sulfur dioxide, nitrogen oxides, ozone, hydrogen sulfide, acetic acid, and formic acid, but there are other gases than can harm collection materials. The field of air quality monitoring in cultural heritage environments is constantly evolving, as is evidenced by recent findings that sealant materials used for display cases produced piperidinol-based compounds. These compounds were not previously known to react with cultural materials, but were found to produce visible corrosion on collection objects (Newman, et al. 2015, Stanek, et al. 2016). If a specific pollutant is defined as an issue in a collection or if it has been determined that a particular compound should not be adsorbed, then it may be beneficial to consider the selectivity of the chosen adsorbent. A more general adsorbent could be considered if the air composition is unknown, but some general adsorbents can have difficulties collecting the previously listed “important pollutants”. For example, non-impregnated activated carbon is known to only weakly adsorb formic acid (Rigbrant 2019). If desired, air quality analysis can be performed using a number of available tools and services. Information on how to execute air quality studies in cultural heritage environments can be found in other published documents (Grzywacz 2006, Tétreault 2003, Canosa et al. 2019)

Adsorbent selectivity may be of interest for certain cultural heritage applications. For these cases, one can consider adsorbent features such as pore size, polarity, and composition. Selectivity describes the adsorbent’s ability to attract or let through specific compounds or classes of compounds. A highly selective adsorbent may only take up specific compounds based on their size or bonding characteristics with the adsorbent surface. For adsorbents that work through physisorption, pore size is an important consideration. As has been discussed, activated carbon, silica gel, and activated alumina all have a wide distribution of pore sizes. Zeolites and molecular sieves have very well defined, uniform pore sizes. Polymeric adsorbents can display either characteristics depending on the synthesis process. Adsorbents with a range of pore sizes often adsorb a wider range of compounds. This may be beneficial for cultural heritage environments in which the air composition is not well defined and varies depending on the materials present. It may also present problems such as the issue with adsorption of volatile plasticizer from cellulose acetate materials (Shashoua, Schilling and Mazurek 2014). Zeolites often have more limited adsorption capabilities depending on the pore size, which may be beneficial for more selective adsorption applications. Selectivity is also influenced

by adsorbent polarity. Polar materials tend to adsorb polar gas molecules and nonpolar materials tend to adsorb nonpolar gas molecules. Finally, chemical composition of the adsorbent affects performance. While the composition of physisorbing materials can affect the gas molecules it attracts, chemisorbents are more known for their selectivity. Adsorption will only occur on a chemisorbing surface if a chemical reaction is favorable. Impregnating an adsorbent such as activated carbon or activated alumina can enhance its ability to adsorb specific compounds. Some publications have included charts containing information about the specific pollutants that different adsorbent materials can adsorb (Tétreault 2003, Muller 2011, Grzywacz 2006, Shepherd 2001).

At a certain point, an adsorbent will reach its equilibrium capacity for adsorption and will become saturated. It can be difficult to predict the point at which an adsorbent will reach capacity in real life, mixed-gas conditions. Nonetheless, choosing an adsorbent with a good capacity for the target gases is important. Capacity can be experimentally determined, as discussed under *Capacity and isotherms*, but such tests are not easily performed in most cultural heritage institutions. Capacities for certain adsorbent-adsorbate systems may be found in research articles or through consulting adsorbent manufacturers. Additionally, it is best if the capacity is determined using partial pressure (gas concentration) values and temperatures similar to those found in the applied environment. Capacity measurements are usually performed using a single adsorbate, and the experimental results may not mimic real life performance. When an adsorbent reaches capacity, it must be replaced or regenerated. Physisorbents can typically be regenerated while chemisorbents cannot without losing their chemisorbing properties. Some chemisorbents may require disposal as hazardous waste. Physisorbents may therefore be a more economical choice for heritage institutions. As a general note, not all adsorbed compounds are easily desorbed during physisorbent regeneration. Desorption depends on factors such as the pore size and bonding characteristics between the adsorbent and adsorbate. It is important to consult the adsorbent manufacturer or a service provider concerning regeneration costs and feasibility.

Adsorbent amount, lifetime, and placement

Determining the amount of adsorbent to use and when to replace it is one of the most sought after air quality questions in cultural heritage environments. Unfortunately, such questions are not easy to answer because heritage environments are so varied in their composition and needs. As a starting point, Tetreault developed an equation to help determine the quantity of an adsorbent needed to maintain pollutants inside an enclosure below a specific concentration (Tetreault 2003):

$$Q = (C_O VN + ES)t / (PC_I)$$

where
Q = quantity of sorbent recommended (g)
C_O = concentration of the pollutant outside the enclosure ($\mu g\ m^{-3}$)

V = net volume of air in the enclosure (m^3)
N = air exchange rate (1/day), normalized to the pollutant of interest
E = area-specific emission rate of the polluting material ($\mu g\ m^{-2}\ day^{-1}$)
S = exposed surface of emitting material (m^2)
t = minimum number of days the pollutant concentration inside the enclosure must be maintained below C_I (days)
P = specific sorption capacity of the sorbent ($\mu g\ g^{-1}\ \mu g^{-1}\ m^3$)
C_I = maximum allowed concentration of the pollutant inside the enclosure ($\mu g/m^3$)

The sorbent layer in the above model is assumed to be ≤ 2 cm thick and well spread through the enclosure. It is the only significant sorbent present and the difference in pollutant concentration between the outside and the inside of the enclosure is at least one order of magnitude. Parmar and Grosjean estimated some values of P for activated carbon inside typical display case environments (Parmar and Grosjean 1989, Tetreault 2003):

- Acetic acid: 5.2 $\mu g\ g^{-1}\ \mu g^{-1}\ m^3$
- Hydrogen sulfide: 7.5 $\mu g\ g^{-1}\ \mu g^{-1}\ m^3$
- Nitrogen dioxide: 7.9 $\mu g\ g^{-1}\ \mu g^{-1}\ m^3$
- Ozone: 5.2 $\mu g\ g^{-1}\ \mu g^{-1}\ m^3$
- Sulfur dioxide: 5.1 $\mu g\ g^{-1}\ \mu g^{-1}\ m^3$

If such calculations are not possible for a particular environment, one can determine the amount of adsorbent needed through consulting other cultural heritage institutions with similar issues, consulting with adsorbent manufacturers, or simply through trial and error.

As discussed, the lifetime of an adsorbent is dependent on its equilibrium capacity under certain conditions. While this equilibrium capacity can be experimentally determined, its application to real-life situations is limited, particularly in situations where pollutant quantities are unknown. The situation is further complicated by the fact that many adsorbents do not visually indicate if they are saturated. Some silica gels contain dyes to show that they are hydrated, and some chemisorbing materials will visually change when they have become exhausted. More common adsorbents like activated charcoal, plain silica gel, and zeolites will not show any indication of saturation. The point at which regeneration or replacement is necessary can be determined by monitoring the adsorbent environment periodically for moisture content or pollutant concentrations. Appropriate tools include hygrometers, passive air sampling devices, or metal coupons. Some passive air sampling devices and metal coupons can be mailed to laboratories for pollutant concentration analysis or visually analyzed in-house. One particularly popular and affordable tool for detecting pollutants in cultural heritage environments is the acid detector (AD) strip. It is a strip of paper dyed with bromocresol green dye that changes color when exposed to acid vapors. The unexposed paper has a blue color and will change to green or yellow upon exposure. Such vapors include acetic acid, formic acid, hydrogen sulfide, nitrogen dioxide, carbon dioxide, and sulfur dioxide. The color of the strip is visually analyzed. Such a strip could be placed beneath a layer

of adsorbent or in the treated environment every so often and checked after one week. A color change potentially indicates that the adsorbent is no longer adsorbing acid gases. It should be noted that AD strips will change color when exposed to light and will slowly react to carbon dioxide. Further information on air quality monitoring techniques can be found in the conservation literature (Grzywacz 2006, Canosa, et al. 2019). If such measurements are not possible, one can consult other cultural heritage institutions about their regeneration and replacement practices, or develop a practical routine (e.g. replacement once per year).

Adsorbents should be appropriately placed for maximum effectiveness, if possible. Ideally, adsorbents should be situated in a thin layer with a large exposed surface area. There should also be some air circulation near the adsorbent. If visibility is an issue, such as in a display case, adsorbents can be placed in hidden trays above or below the display area, ideally with a small fan for air circulation. When determining placement one should also consider other materials that can adsorb pollutants. Surfaces of display cases or storage containers will likely adsorb pollutants, which may be beneficial. Collection objects can also act as pollutant sinks. This may be an issue if an object is particularly sensitive to a pollutant, for example, silver in an environment with hydrogen sulfide gas. In such cases, it may be beneficial to place adsorbents close to the collection object in question to reduce the likelihood that the pollutant will adsorb onto the object surface. In some cases, it may be beneficial to wrap particularly sensitive objects in activated carbon cloth. This can act as a barrier layer between atmospheric pollutants and the collection object. Care must be taken in such situations, though, as carbon cloths (and other carbon products) tend to produce black dust and may contain chlorine compounds. In general, the chemical composition of an adsorbent should be considered during placement, particularly if contact is required between adsorbent and collection object. Some adsorbents contain highly alkaline compounds (potassium hydroxide, KOH) or strong oxidants (potassium permanganate, $KMnO_4$). As a general rule, collection objects should not come in direct contact with strong bases or oxidizers. Thus, mats, filters, or granules containing such compounds should not touch objects. Understanding the chemical composition of adsorbents is also important for the health of staff that handles the materials.

Active vs. passive adsorption

In heritage environments, adsorbents are used under active or passive conditions. Active conditions involve the use of forced air and are generally used in larger spaces such as galleries or storage rooms. In these environments, active pollutant adsorption occurs through installed HVAC systems or portable filtration devices. Active adsorption can also occur inside display cases if air is forced through the adsorbent. Active media typically comes in the form of a filter or packed cartridge that can be fitted inside an HVAC system or portable device. If placed in a display case with a fan, the sorbent can be in the form of a filter, but also as loose granules in a tray or breathable enclosure. Passive adsorption does not involve the use of forced air, rather relying on natural diffusion of pollutants into the sorbent. This

process can include the use of a fan to help circulate air. It is often used in storage containers or display cases in the form of cloth, foam, or loose granules in a tray or breathable enclosure.

Mechanical, or forced, ventilation through an HVAC system involves controlling outdoor air by an air-handling unit that adjusts for excess humidity, dust, and pollution. This review only focuses on filters for gas-phase pollutant adsorption, but further information on dust and humidity control can be found in literature including the 2015 ASHRAE (American Society of Heating, Refrigeration and Air Conditioning Engineers) Handbook - HVAC Applications, Chapter 23: Museums, Galleries, Libraries and Archives (Tetreault 2003, ASHRAE 2015). In order to filter volatile pollutants, the HVAC system must be fitted specifically for gas media (sometimes referred to as chemical or molecular filtration). If high performance filtration is needed, a two-stage sorbent system or a combination of different sorbents may be required. As a general note, electrostatic air filters are not recommended for heritage applications as they produce ozone. If an HVAC system cannot be incorporated into a building, portable air filtration units may be appropriate for adsorbing pollutants in a single room. Active filtration can also be incorporated in enclosures such as display cases, and are either internal or external systems. Internal systems use recirculated air from inside the case that is forced through filters using a fan. External systems are used when a display case is not airtight, as it forces air from the surrounding room into the enclosure. The positive pressure created inside the display case causes the air to ventilate out through gaps. If there are high levels of pollutants inside a display case, active systems are more effective at reducing pollutants than passive systems, but are known to exhaust the adsorbents at a faster rate (Tetreault 2003).

During passive filtration, sorbents are placed in the same enclosed space as collection objects. The pollutant removal process can be viewed as a competition between gas deposition on the objects or on the sorbents. When used inside display cases, it is often desirable to hide the adsorbents by placing them in compartments above or below the display area. In this case, it is a good idea to provide good air circulation by creating openings between the compartments and the display space and even incorporating a small fan near the adsorbents. Some indoor air quality studies have investigated the effectiveness of passive pollutant adsorption. For example, wall panels made of activated carbon, gypsum, and manganese oxide were used to passively reduce indoor ozone and formaldehyde concentrations. Laboratory and field tests of the panels showed that they were successful in reducing the concentrations of ozone and formaldehyde without forced airflow (Sekine and Nishimura 2001, Kunkel, et al. 2010, Gall, Corsi and Siegel 2011). Removal effectiveness was strongly dependent on the exposed surface area of the panel and the adsorbent material. It was weakly dependent on the air exchange rate of the room or test chamber, but it was noted that elevated air speeds were needed to achieve significant (> 80%) adsorption (Kunkel, et al. 2010). With this in mind, adsorbents in passive cultural heritage environments are best used in thin layers over a large area and under conditions with some air circulation, if possible.

Survey of adsorbent use in Swedish cultural heritage institutions

A survey was sent to Swedish cultural heritage institutions in 2018 about their experiences with adsorption materials. The survey was distributed through electronic mailing lists, social media posts, and personal contacts. The target audience was people who care for or help to preserve cultural heritage collections, including collection care managers, preservation specialists, and conservators. Over 180 responses were received from institutions of different sizes that included museums, historical buildings, and archives. The purpose was to understand the extent to which Swedish institutions use adsorbents, the types of adsorbents used, and questions that people have about adsorbents.

The first question focused on whether or not institutions use adsorbents. Example materials were provided, including activated carbon, silica gel, zeolites, and ventilation filters. The results indicated in Figure 2 show that the majority (over 85%) of respondents have never used adsorbents.

Those who answered that they currently or have previously used adsorbents were asked to describe the types of adsorbents and their placement. Answers are indicated in Figure 3.

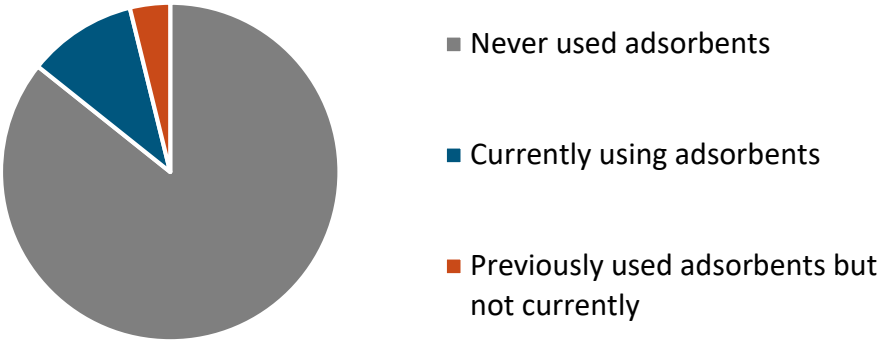

Figure 2: Survey results from question asking institutions to describe their experience with adsorbent materials.

Activated carbon use inside display cases appears to be the most popular in the surveyed institutions, which is consistent with current conservation literature.

For those who answered in Figure 2 that they do not use adsorbents, 67% said that this survey was the first time they had heard of adsorbents. For those who indicated that they are aware of adsorption materials, the majority stated that they do not use adsorbents due to a lack of knowledgeable staff. A section was provided for the survey users to write questions they have about adsorbents, the majority of which focused on the following:

- How effective are adsorbents?
- What do they remove?
- How much do they cost?
- How long can they be used?

It is clear from the survey results that more practical, easily available, and accessible knowledge about adsorbents should be distributed to cultural heritage institutions. Recipients that can benefit from information about adsorbents include conservators, collection managers, preservation managers, conservation scientists, and even estates maintenance or facilities maintenance departments. Preservation and collection management professionals typically deal with smaller scale, passive adsorption situations that directly affect the collection objects. Estates and facilities maintenance services are more likely to work with HVAC gas phase filtration and are often the main contact point for air filter vendors. Maintenance services may not have expertise related to collection preservation or pollution-induced object deterioration. It is therefore important to increase discussion between preservation professionals and facility management professionals for decisions concerning museum air quality. The more knowledgeable institutions are about pollutants and mitigation techniques, the greater their capacity is for making informed collection care decisions.

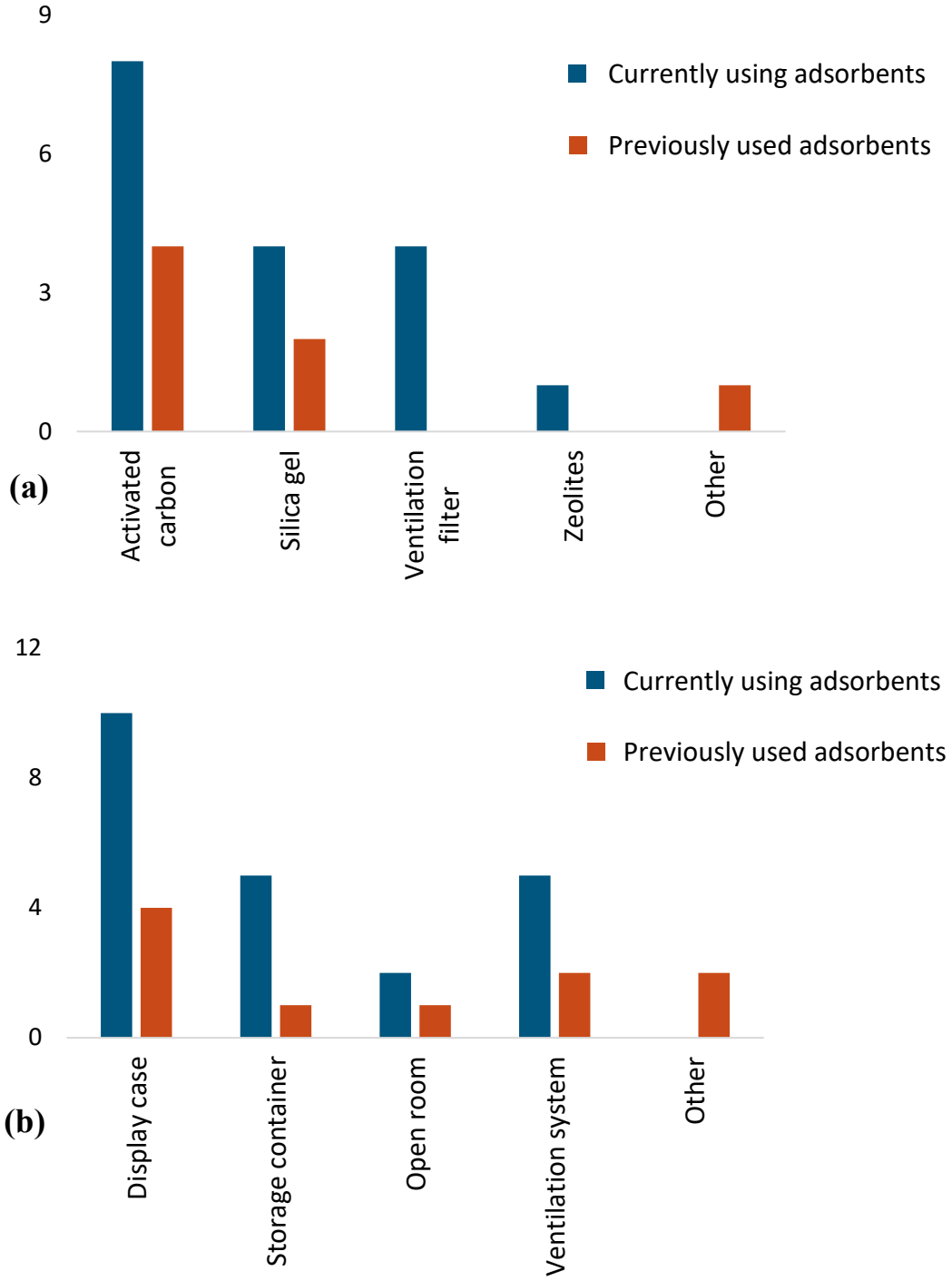

Figure 3: Survey results indicating (a) the types of adsorbents used and (b) adsorbent placement in Swedish cultural heritage institutions.

Zeolite and activated charcoal study

Introduction

Zeolites are mentioned as materials that may be useful for adsorbing pollutants in cultural heritage environments. Unfortunately, there is little information in the preservation literature explaining what zeolites are, their properties, and their effectiveness. In existing cultural heritage studies of zeolites, the authors often do not identify the type of zeolite used, or investigate only a single zeolite. Most technical studies of zeolites perform tests using high gas pressures, which are difficult to correlate to the low airflow, low concentration situations found in spaces such as display cases and museum storage rooms. Additionally, two of the most prominent and corrosive pollutants found in cultural heritage environments, acetic acid and formic acid, are rarely investigated in scientific literature as they are less of a concern in industrial or indoor air applications.

The purpose of this study was to develop a deeper understanding of the properties of some commercially available zeolites and observe how they may behave in cultural heritage environments. Three different zeolite types, 4A, 5A, and 13X were investigated in comparison to granular activated carbon. Each of the three zeolites have different pore (i.e. window aperture) sizes that are uniform throughout the material. Type 4A has a pore diameter of approximately 4 Å, Type 5A a pore diameter of approximately 5Å, and Type 13X a pore diameter of approximately 10 Å. In comparison, granular activated charcoal has a distribution of pore sizes, typically ranging from 10 – 25 Å throughout the material. Zeolites are known for their ability to selectively adsorb molecules based on their size but can also attract molecules to adsorb on their surfaces. For example, zeolite types 4A and 5A used in this study are known for their ability to adsorb highly polar liquids, compounds containing hydroxyl groups, or compounds containing oxygen (Sigma-Aldrich n.d.). Additionally, these particular zeolites are polar materials while activated carbon is nonpolar. Zeolites therefore tend to adsorb more water than activated carbon at room temperature and moderate relative humidity (approximately 50% RH), which may have an effect on their adsorption capacity for other compounds.

Three different types of tests were performed. The first was by Camfil AB and involved forcing low concentrations of acetic acid, formic acid, and toluene through the four adsorbents and measuring their adsorption efficiencies. Acetic and formic acids were studied because of their importance to heritage preservation, while toluene was chosen as a larger-diameter VOC. The second test was performed at Research Institutes of Sweden (RISE) and used headspace gas chromatography – mass spectrometry (GC-MS) to observe the passive uptake of acetic acid by each adsorbent. The final test was a case study in collaboration with the Regional State Archives in Visby (Visby Landsarkivet). It involved measuring acetic acid gas concentrations inside a storage box before and after the addition of adsorbents. The boxes were filled with cellulose acetate negatives, which are

known to produce acetic acid gas as they age and degrade. The gas concentrations were measured with a passive air samplers from the Swedish Environmental Research Institute (IVL) and acid detector strips (AD strips).

While capacity is a very useful parameter for adsorbents, it was not the intent of this study to determine capacity. As pollutant concentrations are low in cultural heritage environments (on the order of parts per billion), capacity measurements would require lengthy exposure times. This could be performed as future experiments. Rather, this study provides a preliminary glance into whether or not common zeolites are worth investigating further for cultural heritage applications, and if there are strong differences between the four adsorbents. The active adsorption study provides efficiency comparisons under a setting where the pollutant is forced through a packed bed of adsorbent. This information is useful for HVAC applications, portable air filters, or specialized situations in which air is actively filtered in a display case. The experiments occurred over several hours, giving an indication of how an adsorbent loses efficiency over time. The passive adsorption study compares the four different adsorbents under a situation with no forced air and generally very little airflow. This replicates conditions often found inside display cases or storage containers. Experiments provide information about the rate at which each adsorbent takes up acetic acid gas, as well as the amount of adsorbate removed from a space over one day. Finally, the case study places the adsorbents in realistic situations to observe their behavior under typical cultural heritage environments.

Materials and methods

Basic properties of the adsorbents and adsorbates used for this study are presented in Table IV and Table V.

Table IV: Properties of the four different adsorbents used in this study.

Adsorbent	Pore size	Polarity	Cation(s)	Particle diameter
Zeolite Type 4A	4 Å	Polar	Na^+	1–2 mm
Zeolite Type 5A	5 Å	Polar	Ca^{2+} and Na^+	1–2 mm
Zeolite Type 13X	10 Å	Polar	Na^+	1–2 mm
Granular activated carbon	10–25 Å	Nonpolar	N/A	2.4–4.8 mm

Table V: Properties of the three different adsorbate gases used in this study.

Adsorbate	Kinetic diameter	Critical diameter (width)	Maximum diameter (length)	Polarity
Acetic acid (CH_3COOH)	4.4 Å (Bowen, et al. 2004)	3.35 Å (NIST 2018)	-	Polar
Formic acid (CH_2O_2)	4.0 Å (Jae, et al. 2011)	4.6 Å (Lourvanij and Rorrer 1997)	4.6 Å (Lourvanij and Rorrer 1997)	Polar
Toluene (C_7H_8)	5.85 Å (Baertsch, et al. 1996)	6.7 Å (Choudhary et al. 1997)	8.7 Å (Choudhary et al. 1997)	Nonpolar

The pores sizes of the adsorbents were not directly measured and are therefore estimates based on available literature (Basmadjian 1997, Yang 1986). Additionally, the term “pore size” for the zeolites refers to their window aperture diameter. As can be seen in Figure 4, the zeolites used are in a pellet shape and the carbon granules are irregular. The zeolite particle diameter therefore refers to the pellet thickness, while the carbon diameter provides the available range of particle sizes.



Zeolite Type 4A



Zeolite Type 5A



Zeolite Type 13X



Activated carbon

Figure 4: Photographs taken of the four different adsorbents used in this study. Photos: Elyse Canosa.

The three zeolites were purchased from Alfa Aesar and the activated carbon purchased from Long Life for Art, the latter a conservation materials supplier. The linear formula for zeolite Type 4A (CAS 70955-01-0) is $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$, for zeolite Type 5A (CAS 69912-79-4) it is $Ca_{/n}Na_{12-2n}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$, and for zeolite Type 13X (CAS 63231-69-6) it is $Na_{86}[AlO_2)_{86}(SiO_2)_{106}] \cdot xH_2O$. All three products are hygroscopic. According to Long Life for Art, the granular activated carbon (type K48) is non-impregnated, made from coconut shells, has an apparent density of 450 ± 25 g/L, and internal surface area of approximately 1100 m^2/g (Long Life for Art n.d.).

Camfil and RISE provided their own adsorbate gases. Camfil investigated acetic acid, formic acid, and toluene; RISE investigated only acetic acid. The diameters of

the molecules in Table V were collected from prior literature (Jae, et al. 2011). Kinetic diameters were determined at the critical temperature or critical pressure of the molecule (the point at which the liquid and gas phase of a substance are indistinguishable). This diameter assumes a sphere shape for the molecule and indicates its size as a target for collision with another molecule. The critical diameter is defined as the diameter of the smallest cylinder inside which a molecule will fit. It also indicates the width of the molecule. Finally, the maximum diameter of a molecule defines its length (Jae, et al. 2011). A value for acetic acid's maximum diameter was not found. Diameter values often differ throughout the literature. The values listed in Table V provide a general idea of the adsorbate sizes in comparison to the adsorbent pore sizes. The diameters of acetic and formic acids are comparable to the pore sizes of both zeolites Type 4A and 5A, indicating that they may have difficulty fitting into their cavities. The diameters for toluene are slightly larger and will not be able to fit through Type 4A and 5A windows. As zeolite Type 13X and activated carbon have larger pore sizes, the adsorbates are more likely to fit into their pores.

Camfil experimental

The experiments at Camfil were performed using the Molecular Media Test Rig located at the Camfil Tech Center in Trosa, Sweden. The test rig consists of five different chambers, four of which contained adsorbents and one of which remained empty. All equipment at Camfil was designed and constructed to be essentially compliant with ISO10121-1 and ASHRAE 145.1 test procedures for evaluating the performance of adsorbent media in general air ventilation applications. Adsorbent test columns used in the Molecular Media Test Rig are smaller than those specified by the standards. During testing, the four adsorbents were exposed in parallel to a test gas (i.e. challenge gas) under controlled temperature and humidity. The control chamber provided upstream gas measurements that indicated the pre-adsorption gas concentration. The challenge gas is also measured downstream of each adsorbent chamber, giving the post-adsorption concentration. Acetic acid and toluene concentrations were measured using an ErsaTec SMART Flame Ionization Detector (FID). Formic acid was measured using a ppbRAE 3000 Photo Ionization Detector (PID). Parameters for each challenge gas is provided in Table VI. The airflow was set to 1.8 m^3/h and the adsorbent bed depth was 26 mm.

Table VI: Camfil test rig experimental parameters for each challenge gas.

Challenge gas	Upstream concentration (ppm)	Average temperature (°C)	Average relative humidity (%)
Acetic acid	6.8	22.2	53.6
Formic acid	11–30 (gradient)	23.7	51.2
Toluene	8.4	22.3	54.0

RISE experimental

The experiments at RISE were performed using headspace gas chromatography – mass spectrometry (GC-MS) and consisted of two separate tests: one that observed uptake rates of each adsorbent and one that measured the adsorption quantity after 1 day. Both tests used 8 mg of each adsorbent in its own 20 mL headspace vial. An empty control vial was also used to measure the amount of acetic acid adsorbed onto the headspace vial walls. The vials were then blown with dry air and closed. A water solution of acetic acid was prepared to bring the relative humidity inside the vials to 50% and the acetic acid gas concentration to a pre-determined level. All experiments were performed using an Agilent 7890/5975 GC/MS equipped with a CTC PAL autosampler for headspace sampling. The autosampler was programmed to withdraw 2 mL of the gas phase from each vial. Gas separation was achieved using a 30 m DB-WAX column (0.25mm diameter, 250µm film) with a temperature program set to 35 °C for 5 minutes, followed by a ramp to 250 °C at a rate of 13 °C/minute.

For the uptake rate tests, 4 to 5 vials were prepared for every adsorbent and each one was measured at a different time interval. All vials were injected with 20 ppm acetic acid at 50% RH and 23 °C and then allowed to stand in the GC autosampler. The remaining gas phase acetic acid concentration inside the vial was collected after certain time intervals and injected into the gas chromatograph. This created a curve following gas phase acetic acid reduction as a function of time. For the adsorption quantity tests, three vials were prepared for each adsorbent at 50% RH and 23 °C. One vial was injected with 200 ppm acetic acid, one with 2,000 ppm acetic acid, and one with 20,000 ppm acetic acid. The remaining gas phase concentration of acetic acid was collected and measured by GC-MS after one day.

Case study at Visby Landsarkivet

The case study at Visby Landsarkivet was performed using AD strips and acid gas passive air samplers from IVL. AD strips are pieces of paper impregnated with bromocresol green dye that changes color when exposed to acid vapors. The strips have a blue appearance prior to use and turn green or yellow depending on the concentration of acid gases present. Analysis is only qualitative. Acid gas air samplers from IVL contain an adsorbent housed in a small plastic cylinder with a mesh lid. Gases diffuse through the lid and into the adsorbent over a given time ranging between several hours to 4 weeks. After the desired exposure time, the samplers are returned to IVL for quantitative analysis by ion chromatography.

Eight lidded storage boxes containing cellulose acetate photographic negatives from the same photographer were used as test spaces. All boxes were the same size (39 x 29.5 x 18 cm), weighed approximately 7 kg, and were made of white corrugated plastic. Throughout the study, all boxes were kept on a shelf inside an archive storage room maintained at 16 °C and 38% RH, and were not exposed to direct light. Figure 5 shows an example of one box used during the case study.

Along the length of each box, a space (approximately 2–3.5 cm wide) was prepared to hold the AD strips, IVL samplers, and adsorbents. The case study was divided into two measurement periods: pre-adsorption and post-adsorption. The pre-adsorption period involved placing 5 AD strips and a single IVL sampler inside each enclosed box for 1 month. Figure 6 (a) shows an overhead view schematic of the placement of the materials inside the boxes, and Figure 7 (a) shows an example box during pre-adsorption setup. After 1 month, the AD strips were removed and analyzed for color change while the IVL samplers were returned to IVL.

Post-adsorption measurements involved placing four breathable Tyvek sachets inside every box. Each sachet contained approximately 65 mL of adsorbent for a total of 260 mL of a single adsorbent per box. The sachets were sealed using a heat sealer. Two sachets per box were hung from the top edge of the box using paper clips while two were placed at the base of the box. Refer to Figure 6 (b) and (c) for placement and Figure 7 (c) for an example of a suspended sachet during post-adsorption. The adsorbents used and their boxes are listed in Table VII.

The adsorbents were placed inside the boxes one week before the AD strips and IVL samplers were added. Similar to the pre-adsorption study, 5 AD strips and a single IVL sampler were allowed to collect inside each closed box for one month before removal and analysis.



Figure 5: Example storage box at Visby Landsarkivet containing cellulose acetate negatives from the same photographer. Eight separate but similar boxes were used for the study. Photo: Elyse Canosa.

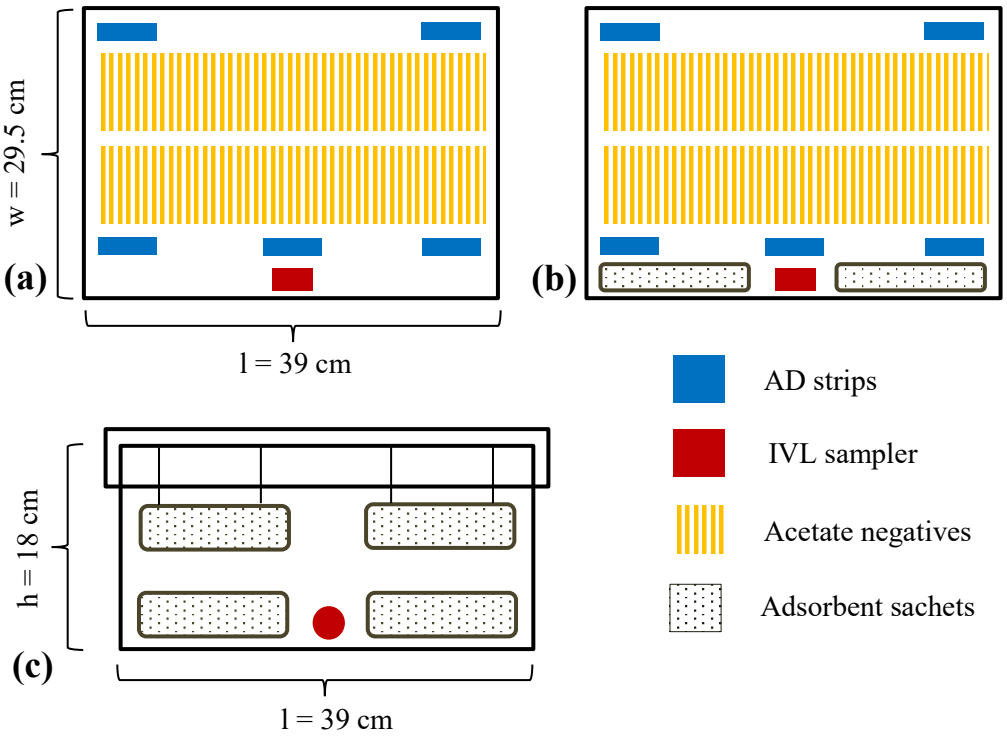

Figure 6: Schematics showing material placement inside the storage boxes during the case study at Visby Landsarkivet. (a) is an overhead view of the pre-adsorption setup, (b) is an overhead view of the post-adsorption setup, and (c) is a side view of the post-adsorption setup.

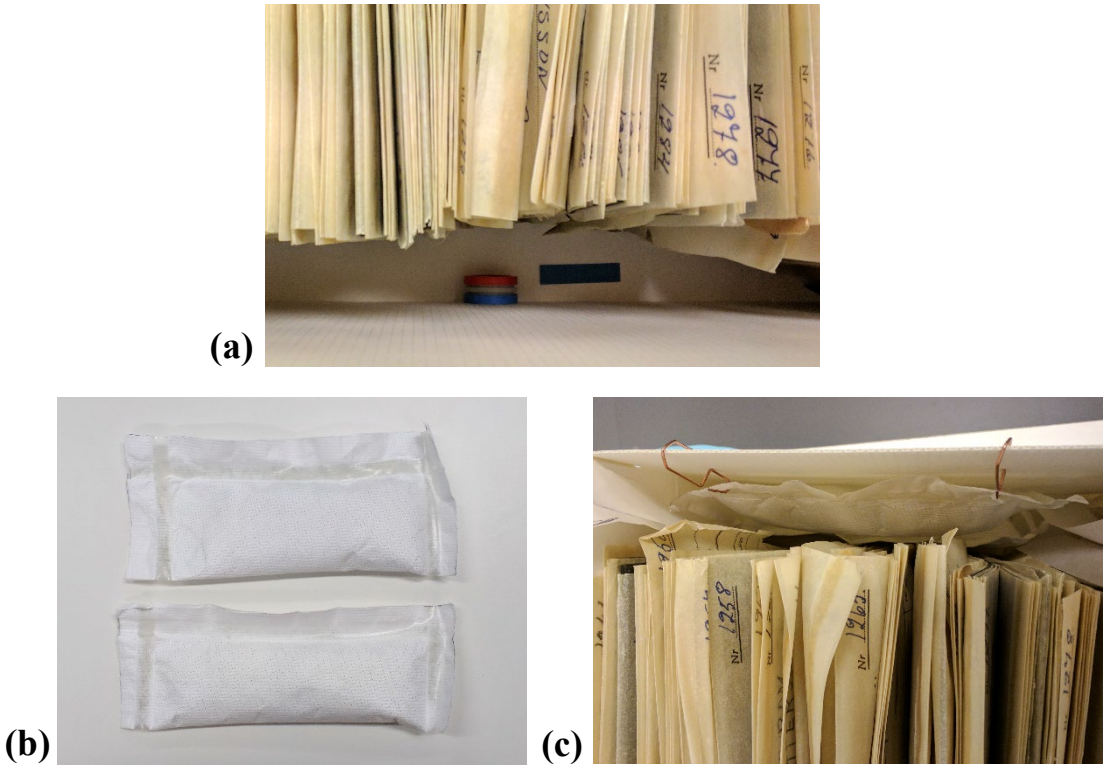

Figure 7: Photographs of the materials used during the Visby Landsarkivet case study. (a) shows the placement of the IVL sampler and an AD strip in the pre-adsorption setup, (b) shows example adsorbent sachets, and (c) shows a hanging adsorbent sachet during the post-adsorbent setup. Photo: Elyse Canosa.

Table VII: The adsorbents and their masses used inside each box during post-adsorption measurements at Visby Landsarkivet.

Box number	Adsorbent	Total adsorbent mass
Box 1	Zeolite type 4A	150 g
Box 2	Zeolite type 4A	150 g
Box 3	Zeolite type 5A	165 g
Box 4	Zeolite type 5A	165 g
Box 5	Zeolite Type 13X	165 g
Box 6	Zeolite Type 13X	165 g
Box 7	Activated carbon	123 g
Box 8	Control (no adsorbent)	–

Results and Discussion

Camfil results analysis

The time dependent measurements for all three challenge gases are presented in Figures 8–10. The downstream (post-adsorption) concentration measurements are indicated in the graphs along with the upstream measurement form the control chamber. The upstream concentration is the maximum measureable challenge gas concentration.

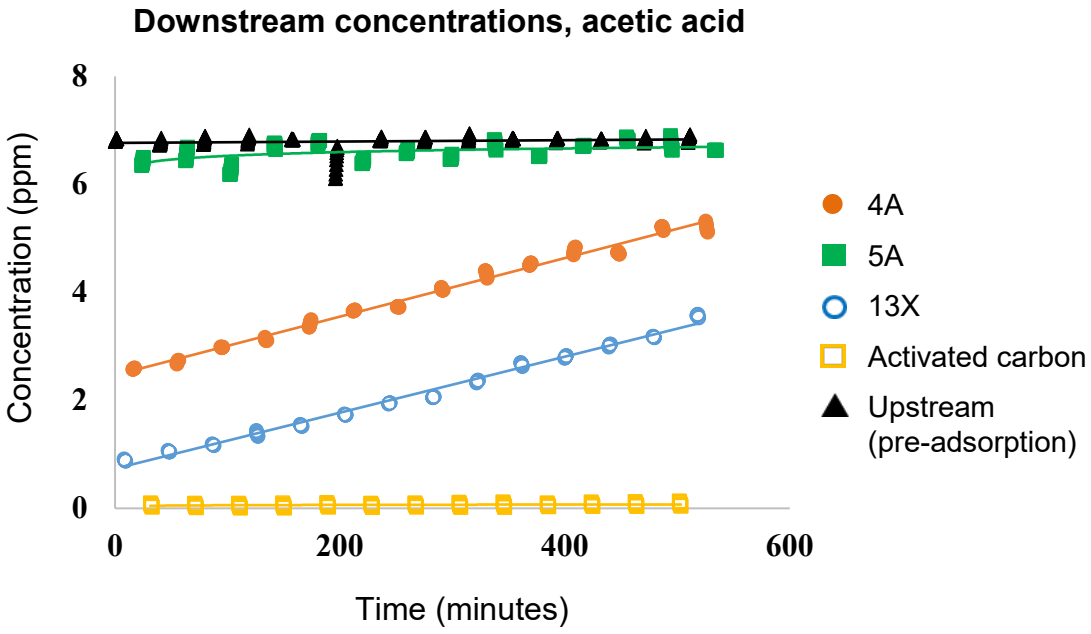

Figure 8: Active adsorption results from Camfil for all four adsorbents and the control chamber (upstream, pre-adsorption). Acetic acid was used as the challenge gas and periodically measured.

In all three tests, activated carbon consistently adsorbed large quantities of the challenge gases, as indicated by downstream concentrations very close to zero. In comparison, the zeolite adsorbents either did not adsorb the challenge gases at all, or began to lose effectiveness as time progressed. The latter situation is indicated by a steady increase in downstream concentration. This could be due in part to the effects of humidity on the adsorbents. As it is a nonpolar material, activated carbon is known to adsorb less water at moderate humidity compared to zeolites (Basmadjian 1997). The challenge gases are therefore less likely to compete with water for adsorption sites on activated carbon. Acetic acid and formic acid are also polar molecules, but less so than water. For comparison, water has a dielectric constant (ε, general indication of polarity) of 80, formic acid of 57.9, and acetic acid of 6.2. Activated carbon can still easily adsorb weakly polar molecules, such as acetic acid, but is known to have difficulty adsorbing formic acid. Finally, activated carbon's nonpolar nature may also be a key factor in the strong adsorption of toluene, as toluene is a nonpolar molecule.

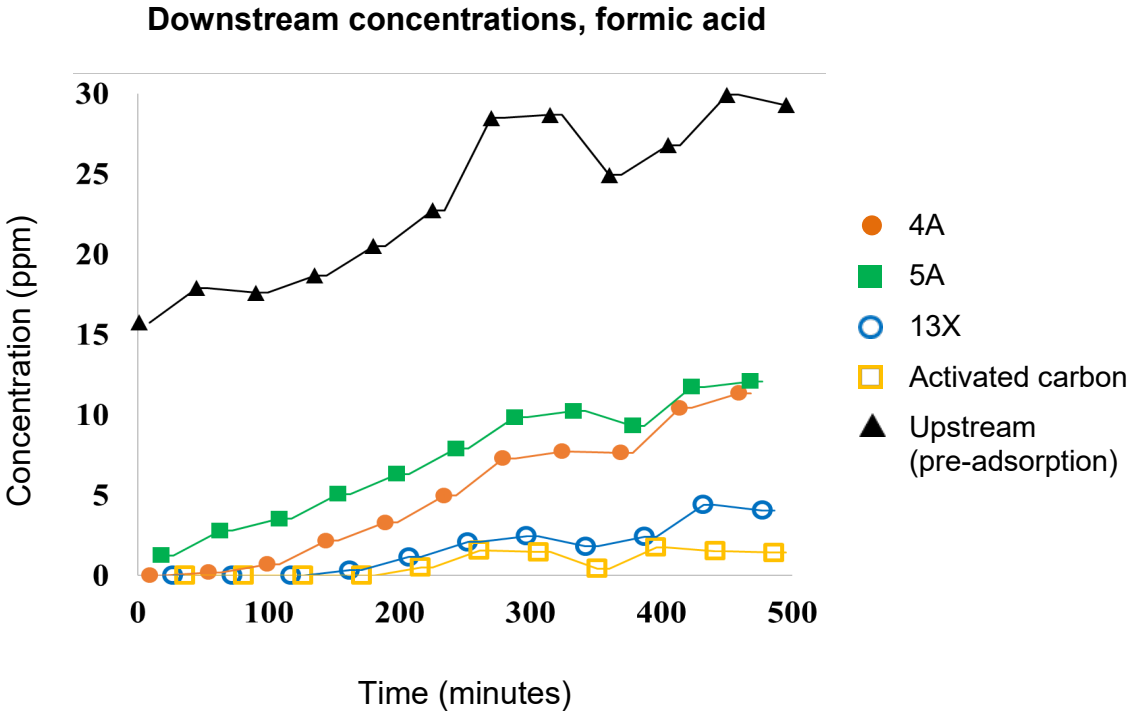

Figure 9: Active adsorption results from Camfil for all four adsorbents and the control chamber (upstream, pre-adsorption). Formic acid was used as the challenge gas and periodically measured.

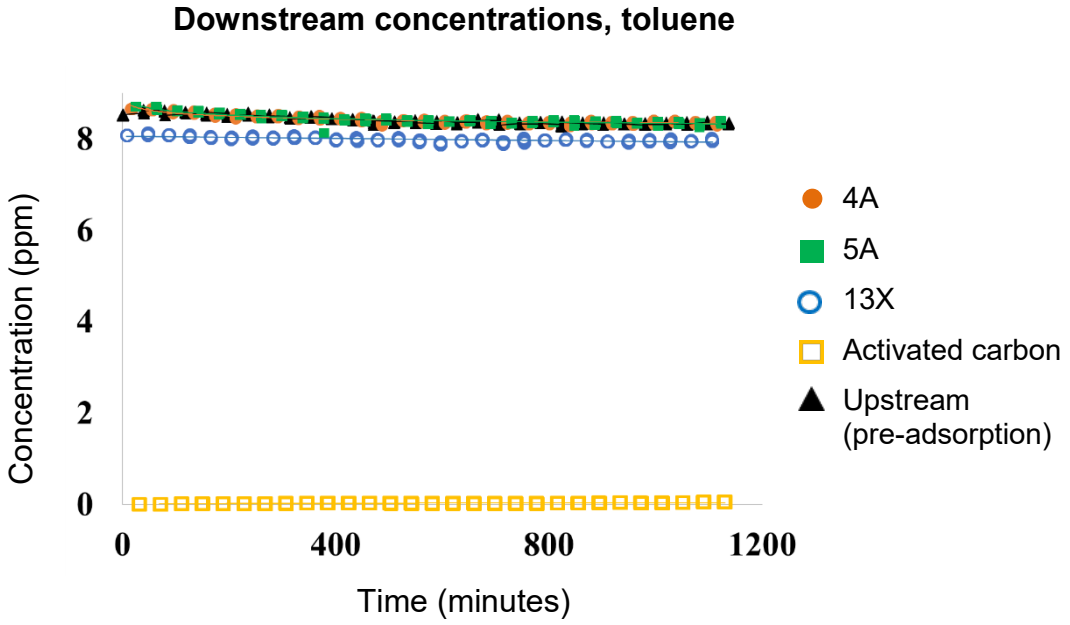

Figure 10: Active adsorption results from Camfil for all four adsorbents and the control chamber (upstream, pre-adsorption). Toluene was used as the challenge gas and periodically measured.

Elemental analysis of the activated carbon was performed at both Camfil and the Swedish National Heritage Board using scanning electron microscopy – energy dispersive x-ray spectroscopy (SEM-EDS). The spectrum from the Swedish National Heritage Board is given in Figure 11. Results from both institutions indicated the presence of potassium, potentially suggesting that the carbon has been treated with potassium hydroxide or potassium carbonate (Rigbrant 2019). This could add chemisorption capabilities to the carbon, increasing its ability to attract polar molecules like formic acid, potentially offering an explanation for the strong adsorption of formic acid in Figure 9. The activated carbon supplier suggested that potassium may be due to minerals found in the coconut shell that the carbon is made from rather than from chemical treatment. This suggestion may be more plausible, as SEM-EDS analysis also indicated the presence of sodium and magnesium, both common plant minerals alongside potassium.

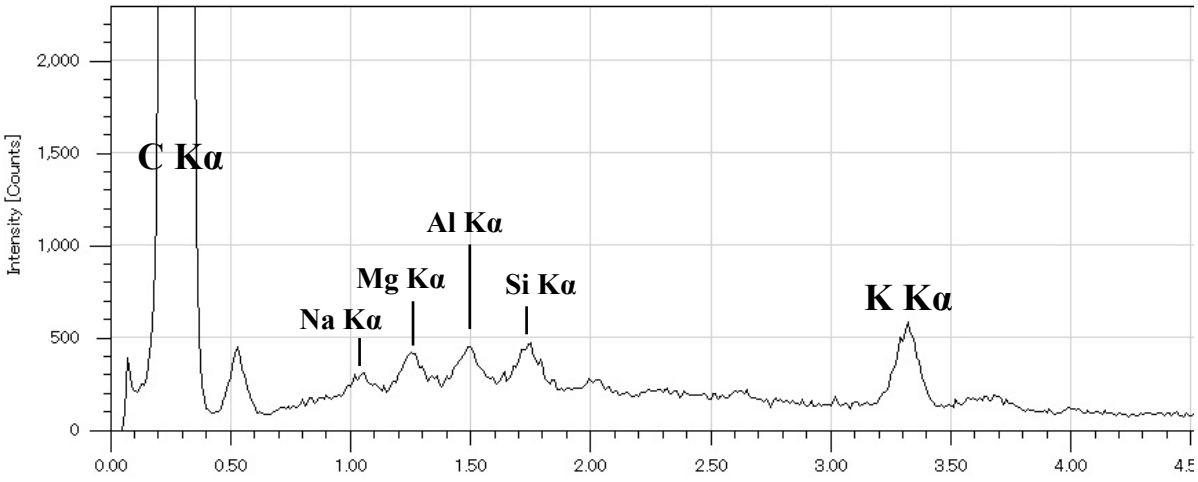

Figure 11: SEM-EDS analysis of the coconut shell activated carbon used in this study.

One general trend among the three zeolites is that Type 13X adsorbs the most, followed by Type 4A and finally Type 5A. The performance of Type 13X in comparison to 4A and 5A could be due to its window aperture size. Type 13X has larger pores than Type 4A and 5A (10 Å compared to 4Å and 5 Å, respectively), and may be more likely to allow the challenge gas molecules through its window aperture. As mentioned previously, both formic and acetic acid molecules are comparable in size to Type 4A and Type 5A window apertures and therefore may have difficulty entering the pores. Formic acid and acetic acid would be able to fit through the window aperture of 13X and access more adsorption sites. Toluene is too large to fit through the window apertures of Type 4A and 5A, but is close in size to the window aperture of 13X. Zeolite Type 13X exhibits a small amount of toluene adsorption, possibly from toluene molecules that were able to fit through the window apertures. Additionally, toluene is a nonpolar molecule and therefore does not adsorb well onto polar materials like zeolites.

Zeolite Type 5A adsorbs both acetic and formic acid less efficiently than Type 4A despite its larger window aperture. This indicates that the size exclusion properties of these two zeolites does not play a strong role in their adsorption of acetic and formic acid. The two challenge gases therefore undergo surface adsorption as opposed to inner-pore adsorption, and their different behavior could be due to their different cations. Both zeolites Type 13X and Type 4A contain sodium cations, while zeolite Type 5A is synthesized with calcium and sodium cations. Some studies have found the presence of adsorbed acetate ions on the surfaces of Type 13X (Narin 2017). One study in particular observed the formation of crystalline deposits when exposed to gas phase acetic acid. The deposits dissolved several hours after acetic acid exposure, but may have been sodium acetate salts forming as the result of interactions between acetate anions and sodium cations. A measured decrease in sodium content of the zeolites after crystal formation supported this hypothesis (Cruz, et al. 2004). The results in Figures 8 and 9 that indicate greater adsorption by 13X and 4A may be due to the greater number of sodium cations in Types 13X and 4A. In Type 5A, many sodium cations are exchanged for calcium cations. While acetate anions and calcium cations can also form salts, this interaction may have been less favorable than interactions with sodium, possibly in part because there is only one calcium ion in 5A for every two sodium ions in 4A.

RISE results analysis

The results for the uptake rate experiments are presented in Figure 12. Acetic acid adsorption to the headspace vial walls was also measured inside the control vial. It was determined that the vial wall adsorption rate was much slower in comparison to the adsorbent uptake rates and has minimal effect on the data in Figure 12.

All adsorbents reduced the headspace concentration inside their respective vials rapidly, decreasing the amount of gas phase acetic acid to sub ppm levels within a matter of minutes. Of the adsorbents measured, activated carbon had the slowest uptake rate. If the presence of potassium in the carbon is indicative of chemical treatment, the slower rate could be the result of chemisorption processes. Such

behavior could also be due to the polar nature of the zeolites and nonpolar nature of activated carbon. Acetic acid, a weakly polar molecule, will be more attracted to other polar surfaces. Additionally, the carbon granules used in these experiments are larger in size than the zeolite pellets, which may also contribute to slower adsorption kinetics. A similar study compared uptake rates of gas phase acetic acid by Type 13X zeolite and activated carbon and found slower uptake rate by carbon in comparison to the zeolite (Cruz, et al. 2008).

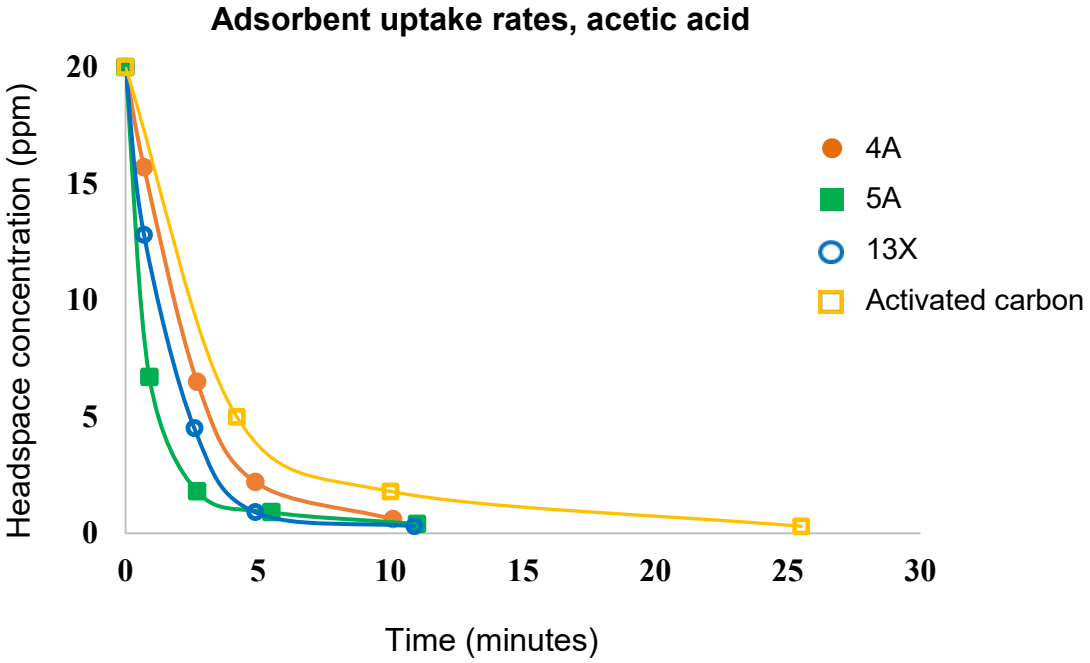

Figure 12: Data from RISE for adsorbent uptake rates of acetic acid gas at 20 ppm. Adsorption of acetic acid to the vial walls occurred but was deemed minimal.

Unlike the active adsorption experiments, all three zeolites managed to adsorb nearly all available acetic acid in the headspace vials, with Type 5A displaying the fastest uptake rate. While initial uptake rate is not indicative of long-term adsorbent behavior, this could indicate that commercial zeolite materials are better suited for passive, low pollutant concentration situations than for active adsorption processes.

The measured data for the adsorption quantity experiments at RISE are presented in Table VIII. For this experiment, adsorption of acetic acid to the vial walls was more significant and therefore could not be ignored, as can be seen under “vial concentration after 1 day” for the control sample. In comparison, adsorption by the four adsorbents was much faster. The calculations in Table VIII for “amount adsorbed by adsorbent” account for the effects of vial adsorption.

For the start concentrations of 200 ppm and 2,000 ppm, all four adsorbents were able to reduce the gas phase acetic acid concentration down to sub ppm levels. Upon exposure to 20,000 ppm, the adsorbents behave differently. Zeolite Type 4A and activated carbon adsorbed the most acetic acid, significantly reducing gas phase concentrations. Zeolite Type 13X was less effective and Type 5A was the least effective of all adsorbents. The behavior of activated charcoal and Type 5A

zeolite in the passive experiments are therefore similar to their behavior in the active experiments.

Table VIII: Data from RISE for the adsorption quantity measurements. Adsorption to the vial walls was more significant and is included under control.

Adsorbent	Vial start concentration (ppm)	Vial concentration after 1 day (ppm)	Amount adsorbed by adsorbent (mg/g)
Control	200	105	–
	2000	1000	–
	20000	9100	–
Zeolite Type 4A	200	0.1	1.1
	2000	0.6	12
	20000	42	130
Zeolite Type 5A	200	0.05	1.2
	2000	0.9	11
	20000	4700	50
Zeolite Type 13X	200	0.1	1.3
	2000	0.04	10
	20000	1600	130
Activated carbon	200	0.2	0.8
	2000	0.3	11
	20000	39	100

Visby Landsarkivet results analysis

Unfortunately, during both pre-adsorbent and post-adsorbent measurements, the IVL passive samplers became saturated due to the high acetic acid concentrations in the box and the long (1 month) exposure time. Useful data from the samplers were therefore not available, but information from the AD strips can still be interpreted. Figure 13 shows the post-adsorption schematic again with each AD strip location identified by a letter that is referenced in Table IX. Figure 14 gives the color code chart that comes with the AD strips. The chart is intended for assessing cellulose acetate film acidity, but is also referenced in Table IX for easy numerical comparisons. A lower pH (and a strip that is more yellow in color) indicates a higher concentration of acidic gases.

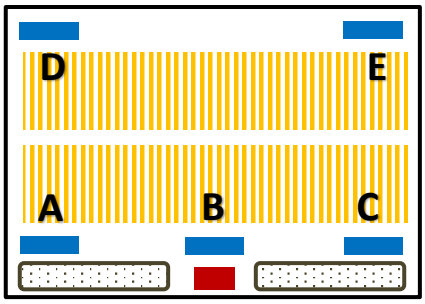

Figure 13: Schematic of the post-adsorbent setup at Visby Landsarkivet with each AD strip location labeled.

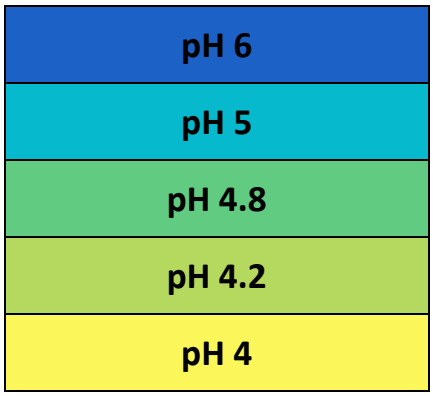

Figure 14: Color code interpretation chart provided with the AD strips. The pH levels are intended to determine the acidity if cellulose acetate photographic negatives, but are also used as numerical references for this study.

Table IX gives the visually assessed pH of each AD strip in the case study boxes. AD strips revert to their original blue color after removal from an acidic environment, thus color and pH must be recorded immediately after removal. From Figure 13 it can be seen that only three of the five AD strips (A, B, and C) are close to the installed adsorbents. This placement is reflected in the results in Table IX. In every box, the pH values for the A and C locations increased in the post-adsorbent assessment, indicating a decrease in acidic gas concentrations. Both of these AD strips are located directly in front of the installed adsorbents. The values for location B (between the two sets of adsorbents) either increase in pH or remain the same, suggesting less of an effect by the adsorbents. Finally, the results for locations D and E are more varied. Most of the AD strips (8 out of 14) in these locations exhibit the same pH pre- and post-adsorbent, while 2 show an increase in pH and 4 show a decrease in pH. This indicates that the adsorbents are only effective at reducing acid gas concentrations in their direct vicinity. As there is very little airflow inside the storage boxes, this result is expected.

Table IX: AD strip data for each box at Visby Landsarkivet for the pre- and post-adsorbent study. Each location refers to the locations indicated in Figure 13.

Box and adsorbent	Location	Pre-adsorbent pH	Post-adsorbent pH
Box 1 – Zeolite Type 4A	A	5	5
	B	4.8	4.8
	C	4.8	5
	D	4.8	4.8
	E	5	4.8
Box 2 – Zeolite Type 4A	A	5	5
	B	4.8	5
	C	4.8	5
	D	5	4.8
	E	4.2	4.2
Box 3 – Zeolite Type 5A	A	5	5
	B	4.8	5
	C	4.8	5
	D	4.8	5
	E	4.2	4.2
Box 4 – Zeolite Type 5A	A	5	5
	B	4.8	4.8
	C	4.8	5
	D	4.8	4.8
	E	4.2	4.2
Box 5 – Zeolite 13X	A	4.8	5
	B	4.2	4.2
	C	4.2	4.8
	D	4.2	4.2
	E	4.2	4.2
Box 6 – Zeolite 13X	A	5	5
	B	5	5
	C	5	5
	D	5	4.8
	E	5	4.2
Box 7 – Activated carbon	A	4.2	4.8
	B	4.2	4.2
	C	4.2	5
	D	4.2	4.8
	E	4.2	4.2
Box 8 – Control	A	4.2	4.2
	B	4.2	4.2
	C	4.2	4.2
	D	4.2	4.2
	E	4.2	4.2

Conclusions

Adsorbents can be very useful for cultural heritage applications. Indoor and outdoor pollutants are a constant threat to the collections, and if used properly, adsorbents can help to reduce such threats. This document explores the theoretical and practical aspects of adsorbents, framing the information for use in cultural heritage environments. It reviews and discusses important technnical terminology such as physisorption, chemisorption, capacity, and desorption to provide cultural heritage professionals with a knowledge base to further explore adsorbents. Additionally, the basic properties of the most common adsorbents (activated carbon, activated alumina, silica gel, zeolites, and polymer-based adsorbents) are presented. Some of the properties cultural heritage institutions should consider when choosing an adsorbent include water adsorption, regenerability, and selectivity. While it can be difficult to determine which adsorbent is most appropriate for a specific application, the information presented in this review can provide a foundation for making such decisions. When implementing adsorbents, many cultural heritage institutions use activated carbon because of its low cost, high availability, low water uptake, and wide adsorption capabilities. While such properties are beneficial for many general heritage environments, it may be of interest to explore more selective adsorbents for specific applications with specific pollutants.

While zeolites have been of interest to the cultural heritage community in recent decades, there is very little information on how different types of zeolites will function under typical heritage environments. This study subjected common commerical zeolites (types 4A, 5A, and 13X) to low airflow conditions, moderate relative humidity (50% RH), and low concentrations of pollutants. The aim was to develop a preliminary understanding of the different adsorption properties of these three zeolites under such conditions. Additionally, activated carbon was used as a non-zeolite comparison material. During the active adsorption experiments performed by Camfil, it was found that activated carbon performed better than all three zeolites when exposed to acetic acid, formic acid, and toluene. Of the three zeolites, Type 13X was most effective, followed by 4A and finally 5A. None of the zeolites adsorbed significant amounts of toluene. Acetic acid and formic acid adsorption by types 4A and 5A may have been due to surface effects rather than molecular sieving effects. During the passive adsorption experiments performed by RISE, the three zeolites had faster acetic acid uptake rates than activated carbon. At lower acetic acid concentrations (200 ppm and 2,000 ppm), all four adsorbents adsorbed similar amounts after one day. At higher acetic acid concentrations (20,000 ppm), the adsorbents exhibited different characteristics, with activated carbon adsorbing the most after one day, followed by 13X, 5A, and finally 4A. The behavior of activated carbon in comparison to the three zeolites may have been due to its nonpolar nature and lower attraction to water at moderate humidity.

The case study did not show significant differences between the four adsorbents, but did reinforce the idea that adsorbents require some airflow to work most effectively in passive situations. This requires some strategic thought about placement in cultural heritage environments. If possible, small fans could be incorporated into rooms to increase airflow. Adsorbents could also be used as a barrier layer. If the source of a pollutant is known, adsorbents could be placed between the pollutant source and the object that requires protecting. In some cases, adsorbents may need to be placed very close to an object that requires protecting. If this is needed, one should avoid direct contact and consider potential interactions between the adsorbent and the object to reduce unwanted reactions. Dust from adsorbents should also be considered as a potential issue. If placed appropriately in passive situations, adsorbents can be used to their full extent.

While zeolites did not perform as well as activated carbon in these studies, they may still have potential for use in situations that require more selective adsorption. The appropriateness for zeolites for a particular situation should be assessed on a case by case basis. Zeolites could also be used for their humidity reduction capabilities if very dry environments are required in cultural heritage spaces. Future investigations of zeolites could include determining their capacities for acetic and formic acid, determining their isotherms under typical heritage environment conditions, and investigating other pollutants.

Appendix

Standards for testing adsorbent performance

ISO 10121-1:2014, Test method for assessing the performance of gas-phase air cleaning media and devices for general ventilation — Part 1: Gas-phase air cleaning media

ISO 10121-2:2013, Test method for assessing the performance of gas-phase air cleaning media and devices for general ventilation — Part 2: Gas Phase Air Cleaning Devices (GPACD)

ANSI/ASHRAE standard 145.1 – 2015: Laboratory Test Method for Assessing the Performance of Gas-Phase Air-Cleaning Systems: Loose Granular Media.

ANSI/ASHRAE Standard 145.2-2011: Laboratory Test Method for Assessing the Performance of Gas-Phase Air-Cleaning Systems: Air-Cleaning Devices

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