Development of adsorbent coatings on thermal conductive structures for adsorption processes

Dissertation zur Erlangung des Doktorgrades der Technischen Fakultät der Albert-Ludwigs-Universität Freiburg im Breisgau

vorgelegt von

Phillip Bendix

Dekanin: Prof. Dr. Hannah Bast

Erstgutachter und Betreuer der Arbeit: Prof. Dr. Hans-Martin Henning

Zweitgutachter: Prof. Dr. Christoph Janiak

Datum der mündlichen Prüfung: 10.07.2019

Die vorliegende Arbeit wurde in der Zeit von Februar 2015 bis Juli 2019 an der Technischen Fakultät der Albert-Ludwigs-Universität Freiburg in Kooperation mit dem Fraunhofer-Institut für Solare Energiesysteme, Freiburg, Bereich Thermische Anlagen und Gebäudetechnik, angefertigt.

"Start by doing what's necessary; then do what's possible; and suddenly you are doing the impossible,,

Francis of Assisi

Kurzzusammenfassung

Die einzige Chance für den Erhalt unserer Erde und deren Biosphäre in ihrer jetzigen Form ist ein schneller Übergang zur nachhaltigen Erzeugung und Nutzung unserer Energie und Ressourcen. Diese Arbeit ist Teil der Forschung zum Erreichen dieses Zieles und beschäftigt sich mit Beschichtungen aus adsorptiven Materialien. Adsorptive Materialien werden unter anderem für Wärmetransformations- und Trocknungsanwendungen verwendet um die Temperatur und Luftfeuchtigkeit in Gebäuden zu regulieren. Ein zentraler Bestandteil der adsorptiven Beschichtungen ist der Binder. Er wirkt als eine Art Kleber während des Beschichtungsprozesses. Die thermischen Belastungen und der niedrige Druck während des Betriebs von Geräten mit adsorptiven Beschichtungen stellen besondere Herausforderungen an diesen Binder. Daher wurden Methoden zur Bewertung der Binder bezüglich ihrer thermischen Stabilität unter Prozessbedingungen sowie der mechanischen Stabilität und des Erhalts der adsorptiven Fähigkeiten der Beschichtungen ausgewählt und etabliert. Eine Auswahl an silikonbasierten und anorganischen Bindern wurde mit diesen Methoden auf ihre Eignung hin charakterisiert. Aufgrund seiner guten Temperaturstabilität, der guten adsorptive Eigenschaften der Beschichtungen und der einfachen Handhabung wurde aus der Gruppe von Silikonbindern Silres® MP50E als der Vielversprechendste identifiziert. Einige der anorganischen Binder zeigten zwar gute thermische Stabilität und Beschichtungen mit guten adsorptiven Eigenschaften, die mechanische Stabilität war allerdings bei keinem der Binder ausreichend für eine Verwendung in der Wärmetransformationstechnik. Mit dieser Arbeit wurde erstmalig eine breite Auswahl an Bindern bezüglich ihrer Eignung für adsorptive Beschichtungen veröffentlicht. Mit dem geeigneten Binder wurde im nächsten Schritt die Beschichtung der Wärmetauscher optimiert. Ziel war es, möglichst leistungsstarke, aber dennoch effiziente Adsorber herzustel-

len. Dazu wurden Proben im Labormaßstab sowie komplette Wärmetauscher mit unterschiedlichen Beschichtungsdicken hergestellt und ihr adsorptives Verhalten umfassend charakterisiert. Zum ersten Mal konnte hiermit gezeigt werden, das es möglich ist die Masse an Beschichtungsmaterial zu erhöhen ohne an Leistung einzubüßen. Es zeigte sich, dass unter den entsprechenden Bedingungen der Wärmeübergang von der Adsorbensschicht auf das Metall des Adsorbers die Leistung begrenzt. Diese Ergebnisse werden jetzt für die Auslegung und den Bau von Adsorbern verwendet.

Im nächsten Schritt wurde der Beschichtungsprozess verbessert um die Herstellung von Adsorbern im industriellen Maßstab zu ermöglichen. Dafür ist es wichtig die Möglichkeit zu haben die Rheologie des Beschichtungsprozesses gezielt zu beeinflussen. Aus einer Auswahl an Rheologieaddtiven wurden diejenigen identifiziert, die für den Einsatz in adsorptiven Beschichtungen geeignet sind. Ihr Einfluss auf die Slurryrheologie wurde umfassend charakterisiert. Eine weitere Verbesserung des Prozesses konnte erreicht werden indem Adsorbentien identifiziert wurden, für die es möglich ist ohne den Einsatz von Ultraschall zu deagglomerieren. Außerdem wurden die zur Verfügung stehenden Beschichtungsverfahren erweitert. Das Spraycoating Verfahren wurde hierzu erstmals für adsorptive Beschichtungen implementiert. Dadurch ist es möglich auf bestehende Beschichtungsanlagen zurückzugreifen und so ein schnelleres Scale-Up auf industriellen Maßstab zu erreichen. Für Beschichtungen mit hoch aufgelösten detaillierten Strukturen wurde gezeigt, dass der Siebdruck von adsorbtiven Beschichtungen möglich ist.

Abstract

The earth as we know it can only continue to exist if humanity finds a way to switch to a sustainable use of energy and resources. This work contributes to the research carried out to achieve this goal by improving the coating of adsorptive materials. These are used in heat transformation and drying processes that allow for efficient temperature and humidity control in buildings.

A central component of these adsorptive coatings is the binder that acts as "glue" in the manufacturing of the coating. In this work the methods to evaluate binder performance regarding their thermal stability under the process conditions, their mechanical stability and their influence on the adsorptive properties of the coating were established. The coatings have to meet special requirements due to the thermal stresses and low pressure atmosphere they experience in these applications. A selection of silicone binders was then characterized with the established tests according to these requirements. Additionally a selection of inorganic binders was investigated because they allow for the use of high desorption temperatures and thus a high energy efficiency of the process. Out of these binders Silres® MP50E emerged as the most promising one due to very good adsorptive properties of the coating, its good temperature stability and ease of use. While some of the inorganic binders showed very good adsorptive properties and temperature stability the mechanical stability of all inorganic binders was not sufficient for their use in adsorption heat transformation technology. This is the first time that a broad selection of binders was evaluated with regards to adsorptive coatings and the results published in literature.

With a suitable binder identified, the next step was to optimize the coating of the heat exchangers in order to work out how to manufacture the most efficient and powerful heat exchangers. Samples with different coating thicknesses were manufactured in small scale and full scale and their adsorption behavior was characterized. It could be shown for the first time that it is possible to increase energy efficiency by improving the mass ration of adsorber to coating and increase the delivered power at the same time. This was shown for small and full scale samples. It was shown that under the corresponding conditions the heat transfer from the coating layer to the adsorber metal substrate is the limiting step in the process. These results can now be used for the planning and construction of adsorbers. With knowledge of a suitable binder and how to coat efficient, powerful adsorbers, the coating process itself was improved to allow for industrial scale manufacturing. A central point here is the ability to control slurry rheology. Out of many rheology additives those that are suited for the application in adsorption heat transformation were identified and their influence on the slurry rheology thoroughly characterized. Additionally the process of slurry preparation could be simplified for several different adsorbents. Here it was shown that the supersonic deagglomeration step is not necessary to prepare a slurry. Extending the possible coating techniques and in addition to the dip

coating process used so far, the spray coating of adsorptive coatings was established for the first time in literature. This process is widely used in the industry and allows for easier plugin into existing coating processes. For the coating of high resolution patterns a proof of concept of the screen printing process was carried out.

Table of Contents

Kurz	zusamment	fassung	I
Abst	ract		III
Tabl	e of Conten	.ts	V
1.	Introduction		
	1.1 Motivation		
	1.1.1	Adsorptive heat transformation	1
	1.2 A	2	
	1.3 C	4	
	1.3.1	Coating slurry	5
	1.3.2	Coating requirements	8
	1.4 Tł	he adsorber	20
	1.4.1	Energy efficiency and power	20
	1.4.2	Heat and mass transfer	23
2	State of the art and literature overview		
	2.1 Bi		
	Direct cr		
	2.1.1	Comparison of direct and binder based coating	
3	Results and discussion		
	3.1 Bi	inder evaluation	
	3.1.1	Characterization methods	
	3.1.2	Binder testing	
	3.2 O	ptimization of metal-to-adsorbent mass ratio	60
	3.2.1	Motivation	60
	3.2.2	Coating of the samples	61
	3.2.3	Characterization	64
	3.2.4	Density of different adsorbents	76
	3.3 Pr	rocess optimization	78
	3.3.1	Rheology	78
	3.3.2	Particle size and deagglomeration	95
	3.3.3	Coating techniques	97
4	Summary		

	4.1	Conclusion and outlook	108
5	Experimental		110
	5.1	Coating	110
	5.2	Porosimetry	118
	5.3	Mechanical testing	119
	5.4	Thermal characterization	120
	5.5	Rheology characterization	122
	5.6	Particle Size	124
	5.7	Density measurements	124
	5.8	Full scale adsorber characterisation – ADSEL Test	124
	5.9	Small scale sample characterization – kinetic test rig	126
6	List of	f Figures	128
7	List of Tables		
8	Abbreviations		
9	List of publications		
10	Eidesstattliche Versicherung141		
11	References142		
Ackno	wledge	ements	150

1. Introduction

1.1 Motivation

How can we lower our carbon dioxide (CO₂) footprint to live in a way that is sustainable for mankind? Researchers around the globe are trying to answer this question and are developing the technologies to solve this problem. The facts are undeniable: CO₂ emissions and the concentration of atmospheric CO₂ are steadily rising as are most other greenhouse gas emissions.¹ A little more than two thirds of these derive from burning fossil fuel for energy production.² In the EU, space heating accounts for 52 % of the residential sector energy demand.³ In warmer climates similar numbers apply to cooling and dehumidification processes and currently around 20 % of the electrical energy worldwide is used for refrigeration and airconditioning. This demand is expected to increase in developing countries during the next decades.⁴ There is a broad agreement in society, science, and politics that measures have to be taken to reduce emissions from these appliances.⁵ That can be achieved by using energy with a low carbon footprint together with process improvements in areas where energy is consumed. This work is part of the latter approach by improving thermally driven adsorption systems. These decrease the energy input used for heating or cooling.

1.1.1 Adsorptive heat transformation

There are several approaches to lower the energy use for heating of buildings such as improved insulation measures and the use of renewable heat sources. Despite the low heat demand of modern buildings, heating units will continue to play a role for a long time.⁶ State of the art condensing boilers work close to the maximum efficiency, their energy yield cannot improve much further.⁷ The next technological step here is the use of heat pumps that draw energy from surroundings sources such as outdoor air for more efficient heating. The sales figures of electrically driven heat pumps have seen a dramatic rise in the last twenty years.⁸ They are able to deliver about 4 times as much heat energy from the surrounding as they consume electrical energy.⁹ While these are impressive numbers and the heating is close to carbon neutral when using electricity from renewable sources, a radical switch from traditional heating to electric heat pumps is impossible since the required electrical infrastructure is not in place yet. Gas adsorption heat pumps are a perfect fit to bridge this gap. They use considerable less energy for the same heat output as a condensing boiler and can tap into the existing gas distribution and storage infrastructure. Energy efficient adsorption heat transformation technologies together with the asset of the mentioned infrastructure and renewable gas production from waste biomass or power-to-gas technologies have the potential to play a major role in future energy scenarios.

1.2 Adsorption heat pumps – working principle

Adsorption heat transformation is based on the adsorption process were a substance from the gas phase is adsorbed to a solid adsorbent, compare Figure 1.1. In adsorption heat pumps or chillers the heat transformation is achieved in a two-step process and needs three different temperature levels. A high temperature level, providing high exergy driving heat (T_H), is used for desorbing the adsorbent. This heat is usually provided at a temperature of 95 °C to allow for a water based, pressure less hydraulic circuit. Future concepts will have to use heat at around 150 °C to improve the process efficiency.¹⁰ A low temperature level energy (T_L) is used as input energy for evaporation of a working fluid. It considered to be freely available from the surrounding air or ground. The temperatures depend on the exact source and climatic conditions but can generally be expected to be somewhere in the range of -5 to 10 °C. The middle temperature level (T_M) lies in between T_H and T_L . The heat at this temperature is delivered by the adsorber and or condenser and used for heating in the case of a heat pump.



Figure 1.1: Schematic representation of adsorption with 1) adsorptive, 2) adsorbate 3) adsorbent, 4) adsorption and 5) desorption.

In the first process step, called the working step (Figure 1.2, left), the adsorptive e.g. water, is evaporated and consecutively adsorbed by an adsorbent releasing heat at T_m . The process is run with only the adsorptive in the gas phase and under reduced pressure allowing for evaporation at low temperatures. The adsorption process takes place until the adsorbent is fully saturated according to equilibrium conditions. The vapor pressure of the adsorptive is assumed to be constant since it is delivered to the gas phase from a reservoir which is kept at a constant temperature level T_L . In the second step, the regeneration step (Figure 1.2, right), the adsorbate is desorbed by heating it up to T_H and condensing the adsorptive at T_m . These three temperature levels are applied in a two-step process taking place in a vacuum tight confined hull. In the heat pump mode, heat at T_M is used to heat the building. It is generated during the adsorption cycle by the heat of adsorption and during the desorption cycle by the energy released during condensation. In the chilling mode the cooling effect arises by conveying heat from the appliance or building to be cooled to the evaporator. The evaporation process cools down the fluid in the hydraulic circuit thus delivering cold to the building.

A gas driven adsorption heat pump consists of several components. A ground or air unit provides heat at the low temperature level T_L . It needs its own hydraulic circuit and pump and is

connected to the evaporator. A condensing boiler produces heat at T_H . In special cases this heat can be supplied by a waste heat stream. The boiler or waste heat source is hydraulically connected to the adsorber. The adsorption module consists of the adsorber – a heat exchanger with the adsorbent on it - and the evaporator. Both are housed in a vacuum tight container. Valves, hydraulic connections and a controller unit are needed as well. This work is going to focus on the adsorber only.





This work will focus on the theory that relates closely to the investigations made here. For further information on the process and the underlying thermodynamics the reader is referred to the following literature:

- Schnabel et al. offer a quick, but thorough insight into the principles and underlying physics of adsorption heat transformation in the chapter "Design and Evaluation" of the book "Innovative Adsorbent Heat Exchangers". Special emphasis is put on heat exchanger design and the heat transfer process in the adsorber.¹¹
- "Characterization of Zeolite-Based Coatings for Adsorption Heat Pumps" by Freni et al. gives a broad overview over the whole range of adsorbent coatings for heat pumps. It covers the choice of adsorbent, their hydrothermal and mechanical stability in depth.¹²

- "Mass transport and adsorption kinetics in porous adsorbent composites for heat transformation applications" by Füldner describes the thermodynamic principles of adsorption processes and the mass transport in the adsorbent and coating layer.¹³
- "Review of Regenerative Adsorption Heat Pumps" by M. A. Lambert et al. gives a detailed overview over the available technologies and compares them to each other.¹⁴
- Henninger et al. summarize existing material choices and corresponding current research activities in their review "New materials for adsorption heat transformation and storage".¹⁵

1.3 Coating

To provide a physical link between the pure adsorbent material and the final adsorption heat pump the material must somehow be incorporated into the adsorber module. This chapter gives an overview of the available techniques and detailed information about the coating technique that was used in this work.

When synthesizing an adsorbent it is usually obtained in powdered form and some kind of shaping is needed. Common shaping processes are granulation to form pellets, extrusion to form monolithic bodies and coating to form a coating layer on supporting structures, see Figure 1.3. Monoliths, extruded bodies of adsorbent, have a poor intrinsic heat conductivity but their low pressure drop makes them suitable for ambient pressure conditions like open adsorption processes.¹⁶



Figure 1.3: Different shapes of adsorbent for heat transfer - pellets or granules (left), monolith (middle) and coating (right).

During the development of adsorptive heat transformation devices, a straightforward approach was to pour adsorbent granules into the gaps between heat exchanger lamellas, the so called fixed bed configuration, see figure Figure 1.4 left. Here the transport of adsorptive in the gas phase to the adsorbent granules is very fast but the generated heat is only poorly conducted to the heat exchanger lamella since the contact points are small and there is no cohesive connection.^{17–20} The heat conduction can be improved by gluing the pellets to the adsorber.

During the 1990's the consolidated bed configuration was of scientific interest. Here the ad-

sorbent is compressed into the void between the heat exchanger lamella, see figure Figure 1.4 middle. ^{21,22} The heat transfer is improved compared to a fixed bed adsorber configuration but mass transport of the adsorptive to the adsorbent is slow and limiting the process.

A coating combines the advantages of these two configurations without their drawbacks, see figure Figure 1.4 right. Mass transport to the coating layer is faster through the gas phase than it is in the consolidated bed. At the same time heat conduction is faster as in a fixed bed due to the large contact area and the cohesive connection.^{17-20, 23-26}



Figure 1.4: Different possibilities of contacting the adsorbent to heat exchanger: granular pellets filled into the adsorber, the fixed bed configuration (left), complete filling of the lamellas the so called consolidated bed (middle) and a coating (right).

There are two distinct approaches for coating the heat exchanger with an adsorbent: binder based coating and direct crystallization.

In the direct crystallization process the adsorbent is synthesized directly on the heat exchanger structure.^{27,28} In the consumptive approach, as used by Fahrenheit AG, some of the heat exchanger metal is oxidized and integrated into the adsorbent during the coating process.²⁹ This results in an intergrowth of heat exchanger substrate and coating and leads to a strong connection between the two. For the binder based coating an adhesive component, the binder, promotes adhesion of the adsorbent particles to each other and to the heat exchanger surface. Binder based coatings were commercially available from Mitsubishi and are used in the Viessmann Vitosorp Models.

An overview of the current literature concerning these coating methods and a detailed discussion about the advantages and disadvantages of binder based and direct crystallization coating is given in chapter 2.1.1.

1.3.1 Coating slurry

For the binder based coating method the adsorbent is applied in a liquid form, the so called slurry. While a powder-coating method is theoretically possible, no processes for adsorptive coatings have been developed so far. The coating slurry consists of three main components: the dispersion medium, the adsorbent and the binder. Additives can be added to refine the slurries properties.

The dispersion medium is a liquid that forms the base of the slurry. Its purpose is to ensure that the slurry is liquid. It is removed by evaporation after the coating process during the cur-

ing step. Usually water is used here because of its low price, general availability and because it is environmentally benign.³⁰ Depending on the binder and adsorbent it might be necessary to switch to organic solvents.

The adsorbent is added in powdered form. Usually it needs to be deagglomerated during the dispersion process to achieve a homogenous distribution in the slurry. The adsorbents particle size distribution and its interactions with the other components and itself determine slurry properties like rheology, dispersability or sedimentation speed.

The binder is the central component of the coating next to the active adsorbent. It must achieve cohesion between the adsorbent particles on the one hand and adhesion of the coating layer to the heat exchanger surface, on the other hand. Depending on the binder-metal and binder-adsorbent combination these cohesion and adhesion forces are based on Van-der Waals forces, dipol-dipol interactions or even covalent bonds.^{31–34}

Polymeric structures and other crosslinking substances are used for this purpose.^{18,19,23,24,26,33,35–37} These can be subdivided in the categories of inorganic, organic and hybrid binders. Examples are shown in Figure 1.5.



Figure 1.5: chemical structure of an inorganic binder - aluminium oxide (corundum) - aluminium in grey and oxygen in white (left), an organic binder – polyacrylate (middle) and a hybrid binder silicone (right).

The class of inorganic binders is characterized by very temperature stable and hard but brittle coatings. Typical uses in the industry are the production of molds for casting of metals or isolating parts in high temperature environments like halogen light bulbs. Material classes are for example silicon oxides, aluminum oxides or yttrium oxides.³⁸ The crystalline or glass like disadvantage.39 structure is the cause of brittleness and their main Organic binders are polymeric organic materials. Their properties can be customized in almost every aspect: During synthesis by altering the chemical structure, the molecular weight, the crosslinking and branching and during manufacturing by changing additives and processing parameters.^{40,41} Traditionally crosslinking oils like line seed oil were used. Modern present day binders are typically polyurethanes, epoxies, polyacrylates or polyesters amongst others.^{42,43} For adsorptive coatings, organic binders are used in the production of open dehumidification adsorption systems. For their use in adsorption heat pumps or chillers it is important that they meet the criteria that will be described in chapter 1.3.2 in detail. Especially the thermal stability has to be ensured since almost all of the organic binders show a limited thermal stability at higher temperatures. This is due to the thermodynamic stability of the prevailing C-C and C-O bonds in the backbone.44 polymer Silicone binders can be thought of as a combination of inorganic and organic binders. The silicone polymer chains consist of a silicon oxide backbone to which organic groups, usually methyl, or phenyl, are attached. The high binding energy of the silicone-oxygen single bonds leads to thermodynamically very stable molecules.⁴⁴ Silicones are applied in many high temperature applications and even made their way into modern kitchens in the form of baking equipment cake pans or parchment paper.⁴⁵

The molecular links of the coating can be created by two different mechanisms – film forming and crosslinking. For film forming the molecules do not react with another but the polymer chains get entangled as depicted in Figure 1.6 top. This happens at elevated temperatures above the glass transition point where the chains are free to move. Such a film forming happens typically in ordinary latex paints and is the case for the Silres® MP50E binder used in this work. For crosslinking binders the molecule chains react with each other forming covalent bonds which results in a very stable network of crosslinked chains, see Figure 1.6 bottom. This is the case for epoxy glue or the Silres® MSE100 binder used in this work.



Figure 1.6: Schematic of polymer molecule chains film forming (top right) and crosslinking (bottom right).

A typical crosslinking reaction is shown in Figure 1.7. The binder molecules are initially terminated by an alkoxy group. This group is then released in a hydrolization reaction and the molecules are now hydroxyl terminated. In subsequent condensation reaction water is released and the silicon-oxygen bond formed. These reactions can be mediated by suitable catalysts like tin or titanium salts. If the polymer chains have more than two of these crosslinking sites available a network will form. In silicones for home use the alkoxy group is often an acetate ester – responsible for the typical vinegar smell during crosslinking.

1



Figure 1.7: Hydrolization of a silicone oligomer and condensation reaction crosslinking the oligomers.

Additives are used to manipulate certain aspects of the slurry. Rheology additives can alter the slurries viscosity and induce shear thinning or thixotropy. Dispersion additives support the deagglomeration and prevent reagglomeration and sedimentation of the adsorbent particles. Defoamers, deareators, wetting additives, anti-fouling additives and many other substances can be added.³⁰ While beneficial at first glance they only help with the coating process and do not participate in the adsorption process of the finished coating. It must be ensured that they don't interact with each other and most of all, that they do not disturb the sorption process in any way.

These components, dispersion medium, binder, adsorbent and potentially additives are combined by mixing to yield the final slurry. This slurry can then be applied in various ways including dip coating, doctor blading, roll-to-roll coating, spray coating or screen-printing. Which of these techniques is applied depends mainly on the geometry of the object to be coated and whether intermediate goods can be coated before assembly or the whole heat exchanger has to be coated. The fabrication of a rotary sorption wheel for open dehumidification is carried out by coating flat metal sheets in a roll-to-roll process after which they are shaped and glued together or by spray coating the whole wheel. In the case of adsorption heat transformation adsorbers, typically a finished heat exchanger is coated in a dip coating process.

1.3.2 Coating requirements

The special conditions in adsorption heat transformation devices make it impossible to use off-the-shelf solutions or products available in the coating industry. Special requirements arising here and their origins in the adsorption process are discussed below.

1.3.2.1 Adsorbent accessibility for adsorptive

A figure of merit in adsorption heat transformation is the adsorptive uptake. It is directly correlated with the produced heat or cold. As shown by Li and others the porous structure of the adsorbent can be obstructed by the binder.³⁷ This results in a lower water uptake. Therefore, when using a binder or any other additive it must be ensured that neither the substance itself nor its possible degradation products reduce the water uptake in a significant way. To characterize the porous structure of the resulting coating, nitrogen sorption measurements can be used.^{12,24,37,46,47} A quantitative conversion of these results to water uptake is not possible but these measurements serve as routine analysis and to categorize the coating into well or worse suited ones. If the adsorbents inner surface and pore volume is lost a high water uptake is not likely. For a binder showing promising results in the nitrogen sorption measurements its water uptake can be expected to be good but should be ensured with water sorption measurements. Additionally to the thermodynamic equilibrium, the kinetics of the process must be considered. The speed of the adsorption process should remain unrestricted by the binder so that the resulting power output is high.

While it is important to keep the pore structure intact and thus the water uptake high, the water uptake per unit volume in the adsorber depends on another factor as well. The higher the binder content in the coating, the less adsorbent is available for the process. In a typical formulation for industrial coatings, the binder content can be 50 %wt and higher to achieve the desired stability.⁴⁸ In adsorptive coatings the binder content must be minimized while keeping the coating mechanically stable. A variation of the binder content has been carried out by Kummer et al. and is therefore not investigated in this work.⁴⁹

1.3.2.2 Thermal stability in low pressure atmosphere

During the adsorption process the adsorber is heated up and cooled down periodically. Typical cycle times in adsorption heat pumps and chillers are in the range of several minutes. Considering around 2000 annual full load hours and a lifetime of 20 years this results in more than one million cycles in the adsorber lifetime. As stated in chapter 1.2 the maximum temperatures during these cycles can be as high as 150 °C. It must be ensured that even under these harsh conditions no gaseous products emerge from the coating. Even minor quantities of volatile substances would pose a threat to the adsorption processes. Adsorbent, temperature and pressure in the confined space of the adsorption module are a fine tuned system that is very sensible to changes. Gaseous substances would change the pressure in this system which will dramatically reduce adsorption kinetics so that the process does not run at its optimum. The gaseous substances could be volatile ingredients that have not been cleared from the adsorber in the curing step and are then released to the system during operation. Another even more probable source for gaseous substances is the chemical decomposition of one of the non-volatile ingredients. Product lifetimes of heating appliances are in the range of 20 years, and a repair or exchange of the adsorption module is not considered standard maintenance. Thermal stability over the whole time must be ensured. Two patented solutions for this problem exist. The patent by Viessman heats up the gas atmosphere and purges the interfering gas together with some of the adsorptive.⁵⁰ Invensor uses a similar strategy but condensates the adsorptive in the purging gas to minimize water loss.⁵¹ Still those solutions are focusing on the symptoms of this problem but not addressing its root cause.⁵⁰ To characterize a binders thermal stability, thermogravimetric analysis (TGA) is used routinely. More complex problems can be investigated with temperature resolved diffuse reflectance infrared Fourier transform spectroscopy (T-DRIFTS) or temperature resolved X-ray diffraction measurements (T-XRD).

1.3.2.3 Mechanical stability

The cyclic process with changing temperatures does not only pose the risk of gaseous substances emerging but puts a lot of mechanical stress on the adsorber as well. Differences in thermal expansion of the metal substrate and the coating must be compensated by the binders and the coatings flexibility to stretch. As stated above, this must be guaranteed for a lifetime of 20 years. The mechanical stability of a coating is a threshold value. It has to meet a certain standard in contrast to values that should be maximized for the coating. Any coating that meets the stability criteria for the application is suitable and any further increase in stability is not necessary. Binders which lead to instable coatings must be identified and to do so the coatings mechanical stability must be assessed. When this work was started, the mechanical performance of the binder was assessed by very basic testing methods. As well there were no investigations of the mechanical stability of adsorptive coatings published in literature so that new test methods had to be established. Testing of the mechanical stability of varnishes and coatings is a well-known task in the coating industry. The tests that were considered suitable for the characterization of adsorptive coatings are described below.

The pull-of test is commonly used in the paint and varnish industry to quantify adhesion forces of a coating. It is described in the norm ISO 4624 – "Paints and varnishes — Pull-off test for adhesion". A handle in form of a stamp is glued to the coating surface. The specimen is then placed into a tensile test machine and the force to detach the handle from the plate is measured.

Cross cut test according to ISO 2409 "Paints and varnishes – Cross-cut test" was considered for mechanical testing since it is a standard method for quality assurance and quality control in the varnish industry. It classifies the coating according to its detachment after cutting with a blade, see Figure 1.9 (top right). Additionally to the assessment of the coatings stability the mode of failure can be determined in the cross cut test. There are two distinctly different failure modes– adhesion and cohesion failure.

For a cohesion failure the detachment of the coating occurs inside the coating layer. The point of failure is the binding force between the coatings particles linked together by the binder, see Figure 1.8 left. This failure mode can often be eliminated or improved by raising the binder

content or by improving the particle-binder interaction. For an adhesion failure the detachment of the coating occurs between the surface of the substrate – usually a metal – and the coating layer, see Figure 1.8 right. Here the binder-surface interaction is not strong enough. This problem can be solved by changing the binder or, as it's commonly done in the industry, by applying an adhesion promoter. This is a very thin layer of a substance that binds well to the surface to be coated and the coating. Often both failure modes occur simultaneously with the other being pronounced. one or more During the time of this thesis the cross cut test has been established independently as a testing method for adsorbent coatings by the Italian "Instituto di tecnologie avanzate per l'energia" -CNR ITAE, confirming its validity for this purpose.¹²



Figure 1.8: Cohesion failure (left) and adhesion failure (right) in a coating.

The resistance of a coating against the bending of the substrate can be characterized by the cylindrical mandrel bending test described in ISO 1519 – "Paints and varnishes – Bend test (cylindrical mandrel)". The sample consists of coated sheets that are bent around mandrels of different diameters as shown in Figure 1.9 (left). The smaller the radius the higher the stress on the coating will be. Since the radii are slightly different for the substrate and the coating, the test replicates the forces experienced during thermal expansion.



Figure 1.9: Cylindrical mandrel bending test (left), impact test (middle) cross cut test (top right), tape adhesion test (bottom right).

The impact test according to ISO 6272 – "Paints and varnishes – Rapid-deformation (impact resistance) tests" characterizes the coatings reaction to shock like stresses. The sample is hit on the backside by a falling weight and deformed, Figure 1.9 (middle). The speed and therefore the impact energy can be controlled by the falling height of the weight.

The tape adhesion test according to ASTM D3330 "Standard Test Method for Peel Adhesion of Pressure-Sensitive Tape" allows measuring the coatings stability quantitatively. A tape is glued onto the coating surface and then peeled off together with the coating while maintaining an angle of 90° as shown in Figure 1.9 (bottom right). In contrast to the other methods that categorize the coatings stability this method measures the actual adhesion or cohesion force.

1.3.2.4 Economic feasibility

The production of traditional heating and cooling devices has been cost-optimized for decades and therefore these devices are sold at very low cost. Even with the ecological advantages, the public will accept only slightly higher price of adsorption heat transformation technology and the higher price must amortize in several years. Especially in markets like in the US, the price usually is the main selling point. Additionally, electrical compression heat pumps, the main competing technology, benefit from years of development in the refrigeration market and can be produced at low costs. To compete under these conditions the economic feasibility of the coating must be ensured and the coating process itself must be optimized. Reproducibility and optimized production cost are the two basic requirements for transferring the developed technique to a commercially viable process. For industrial production the marginal costs of an adsorber mainly dependent on the raw material prices, in particular the heat exchanger and the adsorbent price. These prices probably will drop from their current value with growing numbers of produced adsorbers.

To achieve cost-effective coatings, the coating process must be adapted to existing industrial processes. Especially in the phase with small production quantities a plugin solution that can be used in existing coating facilities is advantageous. When implementing such a process some key points to consider are a proper dispersion of the adsorbent in the coating slurry, a good sedimentation stability of the slurry and the ability to control the slurry rheology.

Dispersion

The adsorbent usually is supplied in powdered form and then mixed with the dispersion medium in the slurry preparation process. Depending on the synthesis and drying procedures as well as the storage conditions the adsorbent crystals can attach together and form agglomerates. During the slurry formation these agglomerates must be broken up into the initial crystals. This is usually achieved by high shear forces applied by mixing devices relying on several different effects. In this work ultrasonic deagglomeration is used as the standard procedure. Depending on the adsorbent only stirring might be sufficient to separate the agglomerates. Determination of the particle size distribution with particle size analysis can be used to check whether the deagglomeration was successful or not. From an economical point of view it is important to know whether conventional stirring is sufficient or more advanced and cost intensive methods have to be used.

Slurry rheology

Rheology, the science of flow, is a key factor in the coating process. Being able to control the coatings rheology is a crucial capability for the successful implementation of industrial scale processes. It is essential to ensure the repeatability or reproducibility of the coating process as these are very susceptible to changes in the slurry rheology.^{52–54} Slurry rheology can be controlled by rheology additives. Nevertheless their use for coating of adsorbers has not been investigated so far.

The basic concept of rheology will be described briefly here. Particular attention is paid to aspects that are relevant to the investigations carried out in this work and therefore re explained in detail. More information on the basic concepts can be found in "Applied Rheology" by T. Mezger.⁵²

A liquids resistance to shear stress is called viscosity. A mathematical description makes use of the model of a liquid sheared between two plates, one moving, and one stationary, see Figure 1.10. While the liquid at the boundary layers at the surface of the plates surface has the same velocity (U) as the respective plate, in between the two plates a velocity gradient $(\partial U/\partial y)$ will develop and friction between the fluid layers moving at different speeds results. To move the upper plate a force proportional to the plates area (A) and its velocity is required, see equation (1). The proportionality factor between force and the product of area and velocity gradient is the liquid viscosity (η). It is measured in the unit Pa·s. Examples of different viscosities are given in Table 1-1 to provide examples of the magnitude and range of viscosities experienced.



Figure 1.10: Model for the mathematical description of viscosity.

$$F = \eta A \frac{\delta U}{\delta y} = \eta A \dot{y} \tag{1}$$

The viscosity is usually plotted against the shear rate ($\dot{\gamma}$). For some liquids their viscosity is not a function of the shear rate they are subjected to. Others have a shear rate dependent viscosity profile. This is important to consider since during most coating processes the slurry

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experiences a range of shear rates and is expected to exhibit the appropriate viscosity behavior during each process step. Table 1-2 gives an example of typical shear rate ranges and their concerning coating process step.

substance	viscosity [Pa·s]
air	$1.8 \cdot 10^{-5}$
water	$1.0 \cdot 10^{-3}$
olive oil	~ 0.1
honey	up to 10^3

Table 1-1: Viscosity values of common substances at 20 °C⁵²

 Table 1-2: Process steps encountered in the coating process and their corresponding shear rates⁵²

process step	shear rate [s ⁻¹]
sedimentation	10^{-3} to 10^{-2}
leveling and running of	10 ⁻² to 1
dip coating	1 to 10^2
mixing and stirring	$10 \text{ to } 10^4$
spray coating	10^3 to 10^4

When classifying a liquids viscosity according to its shear rate dependence, four different types are usually distinguished, three of them are shown in Figure 1.11 left. The simplest form is no shear rate dependence of the viscosity. These types of fluids are called newtonian fluids, the most prominent example is water. Liquids that show a decreasing viscosity with increasing shear rates are called shear thinning or pseudoplastic. The phenomenon is for example observed in blood. The drop in viscosity at high shear rates allows the blood to flow in the smallest blood vessels while keeping the pressure drop low. The opposite effect, an increase in viscosity for increasing shear rates, is termed shear thickening. It can be observed in a solution of corn starch in water. Another shear rate dependent phenomenon is the so called yield point. It can be described as the minimum stress that needs to be applied to make the slurry flow and corresponds to the y-intercept in Figure 1.11 right. For stresses below the yield point the substance will behave as an elastic solid and will reversibly deform. For stresses above the yield point the substance will start to flow. Fluids exhibiting such a yield point are termed Bingham-Fluids, an everyday example is ketchup or toothpaste.



Figure 1.11: Different shear rate dependent behaviours of liquids (left) and yield point for a bingham fluid with the yield point as the y intercept.

Sedimentation and reagglomeration of particles are an issue in the dipcoating process. They are influenced by the low shear viscosity and the yield point.⁵⁵ Slurries with yield points of 10 Pa and above are considered stable against separation of solid and liquid phase.⁵²

The yield point can be determined in several ways – usually the shear stress is measured as a function of the shear strain and the curve is extrapolated to a shear rate of $\dot{\gamma} = 0$ s⁻¹. Different models can be used to fit the data – Bingham, Casson and Herschel-Bulkley are the most common ones.⁵⁶ The Herschel Bulkley model is explained further since it has been used in this work.

The Herschel-Bulkley model uses a power law approach to express the shear stress (σ) as a function of the yield stress (σ_0), the consistency (K), the shear rate ($\dot{\gamma}$) and a shear thinning index (n), see equation (2). The shear thinning index indicates whether the material is shear thinning (n<1) or shear thickening (n>1).

$$\sigma = \sigma_0 + K \dot{\gamma}^n \tag{2}$$

Another measurement method to determine the yield point is the stress ramp method.⁵⁶ Here, the sample is subjected to an increasing stress ramp and the resulting deformation is recorded. As long as the stress is below the yield point the material will not flow and the deformation will remain small. Above the yield point the sample starts to flow and the deformation is much greater. This effect can be observed in a distinct change of the slope in the corresponding plot, see Figure 1.12.

There are some properties that make the yield point hard to measure and especially hard to compare different measurement series. For instance it makes a difference whether the yield point is measured as the minimum stress to make the sample flow - termed dynamic yield stress, or as the shear stress required to maintain flow – termed static yield stress. The appropriate value depends on the application context. For starting to pump resting slurry the dynamic yield stress is the value that needs to be considered. For a pump that just maintains flow the static yield stress is the value of choice. Another point is that some materials such as glass will behave as solids but are in reality a very high viscous liquid. To take into account this phenomenon the term apparent yield stress is used sometimes to describe the measured

effects without claiming to make a scientific valid distinction between a true solid and a high viscosity fluid behavior. In this work the term yield stress and apparent yield stress are used as synonyms.



Figure 1.12: Deformation as a function of the shear stress for yield point determination.

Another rheological phenomenon with importance to the application of coating slurries is the time dependency of their rheology at a certain shear rate. Again, we distinguish two different kinds of liquids. Fluids with a reversible drop of viscosity over time during shear stress are called thixotropic, see Figure 1.13. The effect is for example used in drilling muds. When the drilling is stopped the increase in viscosity prevents the particles in the fluid from sinking to the ground. The other example, a rising viscosity during shearing of a liquid is called rheopexy. It is rarely encountered in nature but its application in protective sports gear or shock absorbing footwear is investigated.



Figure 1.13: Time dependent viscosities of liquids shear stress with the resulting viscosity (left), and a oscillatory-rotatory-oscillator measurement profile.

For the measurement of thixotropy a step function is used. The sample is first characterized at very low shear stresses to record its initial state. It is then subjected to a high shear stress step that disturbs the inner structure and therefore lowers the viscosity. After this step the recovering of the sample occurs, indicated by a rise of viscosity due to reformation of the inner structure.

ture. It is recorded at very low shear stresses simulating a resting solution. The low shear stress steps can be either carried out by a rotatory measurement step at very low shear rates recording the resulting viscosity or by an oscillatory measurement step were the loss and storage module is recorded. For the first case, the rotatory measurement, an exemplified measurement is shown in Figure 1.14. A viscosity plateau for the initial low stress step is observed, followed by a sharp decrease in viscosity for the high shear stress step and a built up of viscosity during the low shear stress recovery step. The time it takes the sample to recover to a certain degree can be used as a measure for its thixotropic behavior.

In the second case an oscillatory-rotational-oscillatory (ORO) measurement is done, illustrated in Figure 1.13 (right). The storage and loss modulus are used for characterization of the initial state in the first oscillatory step. The storage or Young module is the part of the energy that is stored elastically like in a spring. Its counterpart the loss module is the energy that is dissipated like in a dash-pot. In the second measurement step the viscosity drop is observed in a rotatory high shear step and then in the following recovery phase a rise of the storage modulus and a decline in loss module is observed. Here as well the time for a recovery up to a certain degree can be used as a characteristic measure.



Figure 1.14: Measurement profile for a rotatory thixotropy measurement .

Often time dependency and shear rate dependency are observed simultaneously. For coating slurries shear-thinning and thixotropic behavior can be favorable whereas shear-thickening or rheopectic behavior do not play a role at normal adsorbent concentrations. The viscosity is a function of the temperature as well, for most substances the viscosity decreases with rising temperature because intermolecular attraction is getting less relative to the kinetic energy of the molecules.

To achieve a desired rheology profile, rheology additives are used. Common industrial additives are cellulose ethers, polyurethanes or mineral thickeners. Natural additives such as alginates and xanthans are used as well, especially for food preparation. Although readily available from the industry, these additives are not easily applied to the coating process for adsorption heat transformation adsorbers, see chapter 1.3.2

The additives usually work by forming a network on the molecular level inside the solution.⁵⁷ For example bentonite, a mineral thickener, induces shear thinning behavior to the coating slurry. It develops a network in between its crystal particles. The plate like crystals hydrate in

the slurries dispersion media and positive charges accumulate along the particle edges while negative charges accumulate on the particles faces. The electrostatic attraction between the opposite charges of different bentonite particles acts as a link and the particles form a network like structure called house of cards, see Figure 1.15 bottom left.⁵⁸ Agglomerates made from these networks are able to withstand a particular stress and increase the low shear viscosity of the modified solution due to the higher flow resistance. Additionally the agglomerates will enclose some of the dispersion media and immobilize it. When enough stress is applied the network will partially break resulting in a decrease in viscosity because of the smaller agglomerates and because of the release of dispersion medium from within the agglomerates. The mixture behaves as shear thinning. Since the breaking of the links is reversible and they will form again when the shear stress is removed or reduced, the viscosity will then rise.⁵⁷ A similar effect can be observed for flake like particles that do not form a network. Here the resistance to flow is induced by the statistically orientated particles that get aligned to the direction of flow when shear stress is applied, see Figure 1.15 bottom right. The aligned particles show less resistance to flow and this effect induces reversible shear thinning behavior to the dispersion.52,59

Funed silica particles, like the HDK series used in this work, form a network too. The very fine SiO₂ powder consists of SiO_{4/2} tetrahedrons that are connected by siloxane bridges (Si-O-Si). Roughly 50 % of the silicone atoms are terminated with a hydroxyl group. These hydroxyl groups will form hydrogen bonds and result in a strong interaction between the molecules. Through these interactions a 3D-network between the particles will form throughout the dispersion and induce reversible shear thinning behavior.⁶⁰

Other additives work in similar ways. By using the right amount of the right additive or a combination of different additives the rheology of a coating slurry can be adapted to the process demands in certain ranges.



Figure 1.15: Fumed silica network breaking (top), bentonite house of cards structure (bottom left) and reoriantation because of flow (bottom right) .

Other slurry properties that are influenced by rheology additives or the coating slurries viscosity respectively are the settling time and the dispersability of the adsorbent particles. The drag force (F_d) a particle is experiencing can be approximated by stokes law.⁶¹ The force is proportional to the viscosity, the particle radius (d) and its speed relative to the surrounding liquid (v), see equation (3). For sedimentation, gravitational forces are constant so that a higher viscosity results in lower sedimentation speeds. Numerous other variables are a function of the slurry rheology such as levelling, film thickness, surface smoothness or open time.³⁰

$$F_d = 6\pi\eta \, d\nu \tag{3}$$

The influence of rheology on the dipcoating process is described in an idealized model, for a uniform surface withdrawn at a constant speed from a newtonian liquid.⁶² Here film thickness (h) can be expressed as a function of withdrawal speed (U), viscosity (η), density (ρ), gravitational acceleration (g) and a constant (c), see equation (4). The process can be pictured as the interaction between viscous force and gravitational force acting on the liquid. Other forces like inertial forces or surface tension forces can be neglected.⁶³

$$h = c \left(\frac{U\eta}{\rho g}\right)^{0.5} \tag{4}$$

This equation holds true for continuous dip coating and those parts of a workpiece that can be approximated as continuously coated. For a batch process a parabolic thickness distribution along the direction of withdrawal develops due to the slurry drawn to the lower side of the workpiece. It can be mathematically obtained by considering the conservation of liquid vol-

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ume and solving for the film thickness, with t as time and x as the direction of flow, see equation (5) and (6). This shows that a homogenous coating thickness over a piece cannot be achieved with a standard dipcoating process.

$$\left(\frac{\partial h}{\partial x}\right)_t = -\frac{\rho g h^2}{\eta} \frac{\partial h}{\partial x} \tag{5}$$

$$h = \left(\frac{\eta}{\rho g} \frac{x}{t}\right)^{0.5} \tag{6}$$

In general faster withdrawal rates and higher viscosities will lead to thicker coatings, while a denser slurry will result in a thinner coating. While these relationships are useful in many processes the geometry of a heat exchanger is too complex to be described by these easy models.

Summing up it can be stated, that there are four basic requirements for a coating that need to be achieved to meet the requirements of a final product:

- Adsorbent accessibility for the adsorptive the water uptake of the coating should not be decreased neither thermodynamically nor kinetically
- Thermal stability the coating must be thermally stable, it must not emit volatile compounds
- Mechanical stability the coating must be able to withstand the mechanical stresses it is subjected to
- Economic feasibility the process must be cost effective to keep production costs low. One way to achieve this is the integration in existing processes.

1.4 The adsorber

1.4.1 Energy efficiency and power

From a technical point of view there are two main variables that need to be maximized for a good performance of an adsorption heat pump: energy efficiency and the power output. Several measures have been introduced to assess the energy efficiency. The most known to public is the energy rating label provided by the European Union. It ranges from A^{++} for the most efficient heat pumps to G for the most inefficient ones. The rating is based on the ratio between consumed energy and energy output for a predefined load profile. Other measures include the seasonal performance factor – a similar measure that relates the overall energy intake over a year to the output of heating energy, or the primary energy ratio that takes into account the primary energy used to produce the output energy. The efficiency of an adsorption heat pump is typically expressed as the coefficient of performance (COP). The COP is defined as the ratio of energy output to energy input at a set working point. For an ideal process that neglects thermal losses and electric energy used by auxiliary components, the COP

for an adsorber in an adsorption heat pump can be calculated by equation (7). The equation consists of two parts: The numerator sums up the released adsorption enthalpy (Q_{Ads}), condensation enthalpy (Q_{cond}) and the sensible cooling of the adsorber (Q_{cool}). The denominator is the sum of the heat applied for desorption (Q_{des}) and the heat needed for the sensible heating of the adsorber (Q_{heat}).

$$COP_{HP} = \frac{Q_{ads} + Q_{cond} + Q_{cool}}{|Q_{des}| + |Q_{heat}|}$$
(7)

In Figure 1.16, the process is shown in its idealized form in the isosteric diagram. It is subdivided into four steps. Two isosteric steps, (2) and (4), were only sensible heat is exchanged and the adsorber stays on one of the two isosteres X_{min} or X_{max} . The other two steps are isobaric steps, (1) and (3), where sensible and latent heat is exchanged due to the ad- or desorption process and due to evaporation and condensation, respectively. Additionally, sensible heat is exchanged to cool or heat the adsorber in steps (1) and (3).

The quantities used in equation (1) can be mapped to this diagram: Q_{ads} represents the latent adsorption energy from step (3), Q_{cool} the sensible cooling parts from step (2) and (3), Q_{cond} the latent condensation energy of step (1), Q_{des} the latent desorption energy in step (1) and Q_{heat} the sensible heating parts of step (4) and (1). Speaking in temperatures: Q_{heat} and Q_{cool} are made up of the sensible heat exchanged between T1 to T4 and vice versa. Q_{des} and Q_{ads} are the latent part of the exchanged energy going from T3 to T1 and T2 to T4, respectively. Q_{cond} accounts for the condensation enthalpy.



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Figure 1.16: Isosteric diagram of the heat pump process, isosteres are depicted as dashed lines the process as red arrows.

To maximize the adsorbers efficiency the COP must be as high as possible. In regards to equation (7) this means, that the numerator must be maximized and the denominator must be minimized. In order to understand how this can be achieved, the summands from equation (7) are broken down into their contributing elements. We will see that for a given adsorber that is to be coated, the ratio of heat exchanger and adsorbent mass is the only degree of freedom. Adsorption enthalpy can be expressed as the product of water mass (m_{H2O}) and its specific adsorption enthalpy (h_{ads}), equation (8). Taking into account that the water mass is a function of the adsorbent mass and its water uptake during the cycle (ΔX), it can be calculated accordingly. Desorption enthalpy is differently signed but has the same absolute value, equation (9)). The condensation enthalpy can be expressed as the product of the mass of water condensated (m_{H2O}) and the specific condensation enthalpy (h_{cond}) , see equation (10). As in equation (2) the water mass is subdivided into adsorbent mass and water uptake. The energy attributed to cooling is made up of three parts: cooling of the adsorbent, the binder and the heat exchanger. It is the sum of the products of their specific heat capacities (c_p), their mass and the temperature difference (ΔT), see equation (11). For a given binder content x_{Binder}, the binder part is a function of the adsorbent mass. The amount of undesorbed water is neglected. The heating energy can be expressed as the negatively signed cooling energy and the energy needed for heating up the adsorbed water, equation (12). All heat capacities and specific enthalpies are considered to be temperature independent in the temperature range of interest.

p2⁻

$$Q_{ads} = m_{H2O} h_{ads} = m_S \Delta X h_{ads} \tag{8}$$

$$Q_{des} = -Q_{ads} \tag{9}$$

$$Q_{cond} = m_{H20} h_{cond} = m_S \Delta X h_{cond}$$
(10)

$$Q_{cool} = c_{p,s} m_s \Delta T + c_{p,HX} m_{HX} \Delta T + c_{p,Binder} m_{Binder} \Delta T$$
(11)

$$= c_{p,s} m_s \Delta T + c_{p,HX} m_{HX} \Delta T + c_{p,Binder} m_s x_{Binder} \Delta T$$

$$Q_{heat} = -Q_{cool} - m_S X_{max} c_{p,H20(ads)} \Delta T$$
(12)

Although all of these variables can be considered for the optimization of the process, for a given adsorber most of them are fixed. ΔT is given by the operating temperatures and therefore fixed. The adsorbent is given so h_{ads} and c_{p,S} are fixed as well, as is ΔX for a given adsorbent and temperature conditions. The binder and its content are fixed by the choice of adsorbent, making x_{binder} and c_{p,binder} constant. The condensation enthalpy, h_{cond}, is constant. The heat exchanger materials cannot be changed and therefore c_{p,HX} is fixed. For the calculation of the COP the only variables left are the adsorbent mass and the heat exchanger mass. Consequently their ratio dictates the COP and must be optimized. The amount of adsorbent mass should be maximized while the heat exchanger mass should be as low as possible to manufacture highly efficient adsorbers with high COPs.

1.4.2 Heat and mass transfer

Generally it is favorable to have high adsorbent masses to adsorb high amounts of adsorptive in a small volume and to maximize the thermodynamically possible specific energy (Q_{ads}) that can be gained. But there is an important constraint to take into account. To achieve high power outputs (P_{ads}) the process must be fast. The adsorber power is given by the partial derivative of adsorption energy with respect to time, compare equation (13). For characterization of the power the mean power over the adsorption half cycle is used.

$$P_{ads} = \frac{\partial Q_{ads}}{\partial t} \tag{13}$$

If the adsorbent layer is too thick, heat and mass transport in the layer are too slow and therefore the power output is compromised. The power delivered can be expressed as the product of a UA value and a temperature difference, see equation (14). The UA value is the inverse of the thermal resistance of the adsorber. It is given in the unit W/K. The temperature difference is calculated as shown in Equation (15). T_{fluid} is the logarithmic mean of the fluid temperature, correcting for the temperature gradient between inlet temperature (T_{inlet}) and outlet temperature (T_{outlet}) in the adsorber, see equation (6). T_S is the temperature of the adsorbent. Since it is hard to measure it can be calculated from the pressure and actual loading of the adsorbent. The UA value is considered to be temperature independent and consequently the driving temperature difference (ΔT) dictates the course of the power output during adsorption. This mathematical description includes the mass transport in the calculated adsorbent temperature because transport resistances can be understood in terms of locally reduced pressure at the adsorption site. This in turn results in a lower loading which is measured and used as input for the calculation of the adsorbents equilibrium pressure.

$$P = UA \,\Delta T \tag{14}$$

$$\Delta T = T_S(X, p) - \overline{T_{fluid}}$$
(15)

$$\overline{T_{fluid}} = \frac{T_{inlet} - T_{outlet}}{\ln(T_{inlet}) - \ln(T_{outlet})}$$
(16)

To achieve high power outputs, heat and mass transfer coefficients in the coating layer must be high. Small heat transfer coefficients for adsorbers are in the range of $50 - 100 \text{ W/(m}^2 \cdot \text{K})$, while powerful adsorbers have heat transfer coefficients of 250 W/(m²·K) or more. Consequently, the heat transfer coefficient of the coating must be higher or in the same range. The mass transfer in the coating layer must be as fast as or faster than the adsorption kinetics to ensure the local vapor pressure of the adsorptive at the adsorption site is equal to the vapor pressure at the evaporator. The underlying transport phenomena can be subdivided into different steps which are displayed in Figure 1.17. The adsorber is subdivided into coating (1), metal substrate (2) and fluid (3). The mass transport can be considered as two transport regimes – mass transport in the gas phase (a) and mass transport in the coating itself (b). The heat transfer consists of several single steps - heat transport through the coating layer (c), heat transfer from the coating layer to the metal substrate (d), heat transport through the metal substrate (e) and heat transfer from the metal substrate to the fluid (f).



Figure 1.17: Heat and mass transfer in the coating layer with coating (1), metal substrate (2), fluid (3) and mass transport in the gas phase (a), mass transport in the coating layer (b), heat transport through the coating layer (c), heat transfer from the coating layer to the metall substrate (d), heat transport through the metall substrate (e), heat transfer from the metall substrate to the fluid (f).

Depending on the dimensions of the system, mass transport is described by different models. Navier-Stokes equations can be applied for continuous flow in macroscopic dimensions. Gas flow on this scale is not limiting the adsorption process. To identify the region where the Navier-Stokes equations do not apply anymore the Knudsen number is used. It is defined as the ratio of the mean free path of the gas molecules to the characteristic length of the system. Here interactions of the gas molecules with the pore walls play a significant role and cannot be neglected so that diffusive models are applied. Mean free path lengths at the operating pressures of adsorption heat transformation technology are in the range of several micrometers.⁶⁴ Consequently the gas transport in the coating layer is influenced by its macroscopic porosity. A higher porosity will maximize the accessibility of the adsorbent particles and result in faster gas diffusion through the coating layer so that the transport of adsorptive to the adsorption sites is faster and the process is accelerated. On the other hand this porosity is usually accompanied by a loss of heat conductivity which slows down the adsorption process. These are some of the factors that determine the difference between dense direct and porous binder based coatings. Concerning diffusion in the crystals themselves, Stallmach et al. showed that intraparticle diffusion can be estimated by the characteristic time (τ), the diffusion coefficient (D) and the radius (r) with the the following equation (17).

$$\tau = \frac{r^2}{3D} \tag{17}$$

The thickness of the coating layer is proportional to the amount of coating in the adsorber. Therefore, for a given adsorbent a thicker coating will mean more adsorbed water and thus a higher amount of adsorption energy per adsorption half cycle. Thick coatings can be achieved by either coating one thick layer or repeatedly coating several thinner layers on top of each other. The coating thickness is usually not homogenous over the whole heat exchanger. This is especially the case for the dip coating process since the adsorber geometry does not allow for a uniform run off of the coating liquid. Slurry will accumulate in the corners and grooves so that here the final coating will be thicker. A thicker coating is favorable for the absolute amount of adsorbent on the heat exchanger. In equation (8) we see that this increases the numerator in equation (13) and thus power output of the adsorber. At the same time the distance for heat and mass transport increases for thicker coatings which can result in longer adsorption times. This increases the denominator in equation (13) and lowers the adsorption power.

Heat conductivity of the coating is important to remove the adsorption heat from the process. Slow removal of the heat will result in long adsorption cycles. The adsorbent heats up and as a result the equilibrium loading which depends on the adsorbent temperature decreases. While the heat must be conducted through the coating it must as well overcome the contact resistance at the interface between coating and heat exchanger, see Figure 1.17.

Summing up we can state that there is a conflict between amount of adsorbent and heat conductivity on the one hand and accessibility of the adsorbent on the other hand. Investigations concerning this conflict have been carried out by several groups. An overview based on selected works is given in the literature overview in chapter 2.

2 State of the art and literature overview

2.1 Binder based coatings and heat and mass transfer

The following paragraph gives an overview over the published work on binder based coatings and on heat and mass transfer of adsorptive coatings or similar systems. As early as 1984 Kaubeck and Maier-Laxhuber filed a patent on adsorbtive coatings using a binding agent and later a similar patent about the use of a slurry, binder and the drying procedure.^{65,66} In 1988, Restuccia et al. postulated heat and mass transfer as areas that need improvement in the future.⁶⁷ A pellet system was designed and built to study those effects. Power output and heat transfer was characterized for different mass flow rates and temperatures in the hydraulic circuit. The mass ratio between heat exchanger and adsorbent as well as the heat exchangers overall thermal capacity were identified as further areas to be improved. Lang et al. studied heat and mass transfer in compact zeolite layers in theory and experiment.^{17,22} They concluded that the heat transfer was the problem in granular beds while the mass transfer was limiting the process in compacted layers. A binder and melamine or tartaric acid were used to manufacture the compact zeolite layers and as pore forming substances to influence the porosity, graphite was used as a binding agent in pressed zeolite blocks by Pons et al. They studied temperature fronts in these zeolite blocks and concluded once again that the heat transfer from adsorbent to the fluid must be improved.⁶⁸ Pino et al. compared polytetrafluoroethylene (PTFE), graphite and aluminum hydroxide binders regarding their ability to increase the coatings heat conductivity.¹⁸ They concluded that it is possible to improve the thermal conductivity from 0.15 W/(m·K) for 10 %wt PTFE binder by a factor of 2.9 to 0.43 W/(m·K) for 30 %wt or 40 %wt aluminum hydroxide. For graphite the highest heat conductivity was 0.36 W/(m·K) with 40 %wt binder. None of the binders used by Pino, graphite and aluminum hydroxide can be considered to yield mechanically stable coatings. Wang et al. introduced a new approach by synthesizing polyaniline directly on the adsorbents crystal surface which then acted as a binder.⁶⁹ Heat conductivities of up to 0.25 W/(m·K) were measured for 16 %wt of polyaniline binder. Guillemot used inorganic silico aluminates as a binding agent and implemented this mixture in 35 %wt metallic foams to achieve a thermal conductivity of 8.3 W/(m·K).¹⁹ Yanagi et al. presented their findings on heat and mass transfer in consolidated silica gel water adsorption systems.⁷⁰ They showed that the U values more than doubles from 25 to 60 W/($m^2 \cdot K$) when comparing a compressed silica plate to granular bed configuration. The mass transfer was compromised. Zhu et al. characterized and improved contact resistance by 40 % for the heat transfer in pellet adsorbers by gluing them to the heat exchanger - a method that is still used in industrial machines today.⁷¹ Zheng characterized the effect of colloidal silica binders on the catalytic activity of zeolite coatings.^{19,25} In the early 2000's Restuccia et al. did dynamic studies of heat and mass transfer on a coated system stating that these have a comparable good heat and mass transfer, UA-values of 800 W/(m²·K) are postu-
lated for a coating.²³ In this simulative approach the coatings heat conductivity was assumed to be 0.33 W/($m\cdot K$) while grains were assumed to have a heat conductivity of 0.093 W/($m\cdot K$) and powder 0.203 W/(m·K). Marletta et al. further advanced the simulative approach on heat and mass transfer.⁷² They use experimental values of 0.3 W/(m·K) for heat conductivity and 180 W/(m²·K) for the heat transfer coefficient between metal and adsorbent. Tatlier et al. did theoretical studies on the optimal adsorbent thickness for a directly crystalized Zeolite 4A coating looking for the best trade-off between mass and heat transport.^{27,28,73} For the conditions used in that study and the particular type of coating the optimum was found to be between 200 and 400 µm. Cacciola et al. improved the heat conductivity using metal in the adsorptive layer but added a lot of thermal capacity with this approach.⁷⁴ Freni used a bentonite binder to coat salt infused silica gel.²⁶ The power per kilogram adsorbent was raised by a factor of 3.75 from 20 - 40 W/kgs to 150 - 200 W/kgs. In further works he too proved experimentally that coated heat exchangers have higher specific powers than granular bed adsorbers.⁷⁵ Here the mass specific power was raised from 498 W/kg_s to 675 W/kg_s. At the same time the volume specific power of the coated adsorber was only 50 % that of the granular bed adsorber. A silane based coating was used for these experiments. A commercially available option for zeolite coatings was investigated in several publications by Dawoud. The binder used in this system is not publically available.^{76,77} He simulated kinetics of coated DDZ70 layers of 700 and 550 µm in 2007 and compared coated small scale samples to full scale adsorbers. He found, that for thicker coatings the power decreased and postulated a mass transfer limitation. In 2008 he filed a patent on the use of fibers to enhance the mechanical stability of coatings using inorganic binders.⁷⁸ The instability of inorganic binders had not been mentioned by any researcher before but it seems to be an inherent problem of this class of binders. Another patent was filed by Dawoud that included gas forming additives in a coating to increase porosity and thus facilitate mass transport.⁷⁹ Freni too, investigated an adsorber using the commercially available coating and compared it to a "clay based" binder.³⁶ Water isotherms were the same for both coatings and both lost less than 1% loading capacity after 35000 cycles of ad- and desorption. Heyden et al. used polyvinylic alcohol (PVA) as a binding agent.²⁴. Film thicknesses of less than 200 µm were found to yield fast mass and heat transfer.²⁴ While in general, the coating will not get in touch with liquid water, it is questionable whether a water soluble binding agent like PVA is the best choice in a water based system. The same applies to the methyl cellulose binder used by Waskiewicz.³⁵ Schnabel et al. did further investigations on the kinetics of a coated layer in small scale, while Bauer did investigations on kinetics using full scale heat exchagners.²⁰ Direct crystallization and dip coating of SAPO-34 were found to be faster by a factor of 3 compared to glued silica gel granules. In 2012 silicone based binders where published for the first time. A patent was filed by Henninger et al. and Kummer et al. on this type of binder, which was then used in various other pupblications.^{80–87} In the same year Calabrese et al. used the chemically similar silane based zeolite coatings for corrosion protection.³³ In later works, using that class of binders, Calabrese et al. investigated three different types of silanes regarding their application in heat transformation applications and for corrosion protection which was later adapted by Freni et al.^{33,34,88,75} Mechanical stability, wettability and corrosion protection behavior were investigated. Calabrese also postulated the existence of covalent bonds between metal surface, adsorbent and silane binder matrix, but did not provide any scientific proof. Also, Zheng made use of this binder to coat small scale samples and Simonetti used it for works on evaporative cooling.^{25,89} Water uptake was not compromised in these works. Li et al. published one of the few works that do not just use a binder without elaborating the particular reasons, but compared different binders such as an epoxy resin, polyvinyl alcohol or bentonites in an adsorptive silica gel coating for the use in evaporation desalination plants.³⁷ His work focuses on adsorption properties of the coatings, BET surface area and sorption isotherms. The obtained results are only partially applicable to coatings for adsorptive heat transformation since most of these binders do not match the requirements stated in chapter 1.3.2. Nevertheless the highest BET surface area of 397 m²/g was achieved for corn flour binder. The initial adsorbent had a BET surface area of 680 m²/g. An overview of the binders used in all of the publications mentioned above is given in Table 2-1.

Summing up, it can be stated that in most cases the optimization of heat transfer was the main criteria to use binder based coatings. The need for improvement in this area was idenetified early in theory and experiments. It was shown by several independent sources, that a coating improves the performance of adsorptive systems by improving heat transfer of the system. A good overview on the topic and the corresponding literature can be found in the book "Characterization of Zeolite-Based Coatings for Adsorption Heat Pumps" published by Freni et al.¹² Regarding the choice of binders there has not been much work published in literature so far. In this thesis, the analytical methods to assess the coatings performance were developed and established. They were applied to a selection of silicone binders, the most promising group of binders available and to a selection of inorganic binders that work well for very high desorption temperatures. This type of binder allows for very high desorption temperatures resulting in highly efficient processes. Using the best binder identified, heat and mass transfer was characterized and optimized by comparison of small scale samples and full scale adsorbers. The optimal metal to adsorbent mass ratio and corresponding U values were identified and can now be used for the design of other adsorbers.

Author

Binder

		mor gume, or gume
graphite	Pons ⁶⁸	inorganic
polytetrafluoroethylene	Pino ¹⁸	organic
graphite	Pino ¹⁸	inorganic
aluminum hydroxide	Pino ¹⁸	inorganic
polyaniline	Wang ⁶⁹	organic
silico aluminates	Guillemot ^{19,23}	inorganic
silica based	Zheng ²⁵	inorganic
alumina gel	Restuccia ²²	inorganic
bentonite	Freni ²⁶	inorganic
poly vinyl alcohol	Heyden ²⁴	organic
clay based	Freni ³⁶	inorganic
methyl-phenyl-silicone	Henninger ⁶⁵ , Kummer ^{66,85,86} , Munz ⁸⁷ ,	hybrid
	Bendix ^{82,83} , Lenzen ⁸⁴	
silane	Calabrese ^{33,33,34,88} , Freni ⁷⁵ , Zheng ²⁵ ,	hybrid
	Simonetti ⁸⁹	

Direct crystallisation

In the direct crystallization route the adsorbent is directly synthesized on the substrate to be coated. Just as for the binder based coatings, the heat transfer is improved drastically compared to a fixed bed adsorber. Jeremias et. al achieved to raise the thermal conductivity of aluminum fumarate by a factor of 3 to 0.33 W/(m·K). There are several different techniques that can be used to coat a substrate with the desired adsorbent. The simplest approach is to add the substrate to the solution in which the synthesis is carried out.⁹⁰ The substrate can then act as an initial nucleus and the adsorbent will form preferably on the substrates surface. This technique can be refined by using the so called seeding technique.⁹¹⁻⁹³ Here, the substrate is coated with small crystals of the adsorbent using conventional coating techniques. These induce crystal growth of the adsorbent on the substrates surface during synthesis of the adsorbent. The consumptive approach patented by Fahrenheit AG makes use of the metallic substrate which is superficially oxidized in the reaction and becomes a part of the zeolite.²⁹ This leads to a sound connection of coating and substrate and improves heat transfer and stability. Another popular method is to immerse the substrate to be coated into the solution of reactants. While the solution of the temperature is kept constant just below the conditions necessary to form the desired product, the substrate is heated up. The product will be deposited on the substrates surface where the temperature is high enough for its formation, hence the name thermal gradient method or substrate heating method.²⁰ This method has been implemented by Tatlier et al. for the formation of zeolites.^{94,95} They did extensive research on the performance and optimization of these coatings.^{27,28,96,97} The method was then adapted to the synthesis of metal organic frameworks by Jeremias et al. and further refined by Ernst et al.^{46,98,99} For the formation of metal organic frameworks a whole array of other methods has been developed additionally. The layering up technique builds up a MOF coating by repeatedly dipping the substrate into a solution of a linker and then a solution of a metal oxide cluster.¹⁰⁰ The coating is formed monolayer by monolayer. For the anodic route a metallic electrode is submerged in an electrolyte that contains the linker. The electrode is then electrochemically oxidized so that the desired metal oxide is formed and reacts with the dissolved linker to form a layer of MOF on the surface.^{101–103} In the cathodic deprotonation approach the acidic linker molecule is deprotonated by a cathodic reaction and is then available to form the desired MOF.^{104,105} As another option, the synthesis of MOF films can be carried out on a substrate coated with a conducting layer that is then subjected to microwave radiation in a solution of reactants.^{106,107}

All of these methods are well suited for the formation of MOF thin films but their applicability to the production of adsorbers for adsorption heat transformation is questionable since here a thicker film has to be formed to achieve the desired amount of adsorbent. Full scale adsorbers using the direct crystallization approach have been presented by Bauer et al., Jeremias et al., Ernst et al. and Wittstadt et al.^{99,108–112} The commercially available thermally driven adsorption chillers by Fahrenheit incorporate an adsorber that is produced by the consumptive direct crystallization approach.

2.1.1 Comparison of direct and binder based coating

Comparing the direct crystallization approach to binder based coating we can state the following advantages for direct coatings:

- the synthesis and coating are carried out in one single step, potentially saving time and costs
- no binders or additives are used that lower the amount of active content. The coating consists of adsorbent only
- higher coating densities can be achieved, maximizing the amount of material on the adsorber

• especially for the consumptive approach, the coating and metal surface are closely connected to each other, maximizing thermal transport

On the other hand the following disadvantages can be stated:

- the synthesis is often carried out at challenging conditions, like pH, temperature, solvents or pressure. The substrate to be coated must be designed to withstand all these conditions.
- the reaction vessel must be suited to the size of substrate, e.g. a full scale heat exchanger
- after synthesis of an adsorbent in powdered form the product is usually purified by further washing steps. These are harder to carry out on a whole heat exchanger than on a powdered adsorbent.
- Often template molecules are used for the synthesis of the adsorbent and must be removed by a heat treatment step. For direct crystallization the whole heat exchanger has to undergo and withstand the same treatment steps.
- amorphous byproducts might be left in the coating, decreasing the active amount of adsorbent
- the synthesis must be fine-tuned to the adsorbent. Switching from one adsorbent to another means establishing and optimizing a new synthesis
- the dense coatings obtained with direct crystallization limits the achievable mass transfer in the coating layer
- for the consumptive approach the heat exchanger material that is to be consumed must be suited to the synthesis step it is involved in

The binder based coating approach has the following advantages:

- adsorbent synthesized in industrial processes can be used. Adsorbents that are used in big quantities for other processes as well can be obtained very cheaply
- occupational health and safety concerns as well as investment costs that are needed for a chemical synthesis have not to be dealt with since the adsorbent synthesis is likely to be outsourced to a chemical company.
- by choosing an appropriate binder and additives, coating properties like porosity or flexibility can be influenced to match the applications need
- industrial proven coating processes that have been demonstrated in large scales already can be used for the coating step

• switching from one adsorbent to another needs readjustment of the process but is much easier than developing a new synthesis process as it is the case for direct crystallized coatings.

But there are the following disadvantages to mention:

- complex substrate structures are hard to coat and can only be addressed by the dipcoating method.
- the binder and all additives used must be selected carefully to match the operating conditions
- the binder and additives decrease the amount of active material per volume

Summing up we can state that when coating an adsorber the advantages and disadvantages of each method must be weighed against each other and the appropriate method for the problem at hand must be chosen. For experiments with a new adsorbent the binder based route is likely to be easier to implement. For highest demands regarding the volume specific power the direct crystallization approach can have advantages but for commercial processes the binder based route is better suited. The experimental part of this work deals only with binder based coatings.

3 Results and discussion

The results and discussion section is subdivided in 3 parts. The first part deals with the choice of a suitable binder. The second part is about the optimization of the adsorbers efficiency and power by adjusting the coating. The third part discusses the optimization of the coating process with regards to an industrial application.

3.1 Binder evaluation

The first step for the binder characterization was to evaluate which of the coatings properties could be used to assess the binders performances. That included choosing appropriate analytical methods that could be used to quantify this performance. Several testing methods have been considered, will be presented in the following section and will then be used to characterize binder and additive performance in later sections. Detailed information on how the tests were performed as well as on what apparatus and analytical methods have been used can be found in the experimental chapter 5.

3.1.1 Characterization methods

The following methods have been applied to the characterization of adsorptive coatings. The specific challenges when applying the methods to this topic are discussed in the following paragraphs. The results for tested coatings are presented in chapter 3.1.2.

3.1.1.1 Mechanical stability

When this work was started the mechanical performance of the binder was assessed by very basic testing methods. Coated samples were dropped on the lab bench from a height of approximately 30 cm. The coating was then visually inspected for cracks or other failures. Clearly, new methods had to be established. Several testing methods were considered, potential tests selected and evaluated.

Pull-off test

The pull-off test described in chapter 1.3.2.3, and 5.3.4 was the first method that was considered for mechanical testing. During preliminary trials the method showed some drawbacks when used for adsorptive coatings. Due to the coatings macro porosity the glue penetrated the adsorbent surface extending down to the aluminum bottom plate and glued the handle to the bottom plate. The resulting measurements did not measure the stability of the coating but that of the glue. To avoid this problem two plates, glued to handles were joined with the coating in between them. Several specimens were prepared but unavoidable slight misalignment of the stamps resulted in shear forces parallel to the plates when fixing the specimen in the tensile test machine. This caused a preliminary failure of the coating and uninterpretable results.

Even with proper alignment of the handles using a custom made alignment rack the problem persisted. Fixing the handle in a ball joint would be a possible solution but would make the whole test too complicated for practical use so that this testing procedure was considered not suitable to the problem.

Freni et. al. and Calabrese et al. published results that used the pull-off test successfully without reporting problems of glue leaking into the coating.^{12,113} This can probably be contributed to a denser coating investigated in these tests.

Cross cut test

The cross cut test described in chapter 1.3.2.3 and 5.3.2 could be applied to adsorptive coatings. A cut sample with detached coating is shown in Figure 3.1. On the range of GK 0 to GK 6 of achievable results the coating should score zero to three to be safely used in a coating for adsorption heat transformation. Scores of four and higher can be improved by using an adhesion promoter or more binder depending on the failure mode.

Cylindrical mandrel bending test

The cylindrical mandrel bending test described in chapter 1.3.2.3 and 5.3.1 could be successfully applied to adsorptive coatings. Determining the exact radius at which the coatings fail would demand for many samples, resulting in very high costs. Therefore a "fail-or-pass" mode, as provided in the respective norm, ISO 1519, was used. Here the specimens are subjected to testing at different radii and the coating is inspected for failure. Radii were chosen to be 32, 16, 8 and 4 mm. This is on the unchallenging side of the scale. In their application in adsorbers for heat transformation applications the coating is experiencing repeated stress but the amplitude is low. Coatings failing at a radius of 16 mm or below can be considered suitable for the application in coatings for adsorption heat transformation. Stability demands would be higher if the substrate was coated as a semi-finished product and had to undergo stresses during assembly of the adsorber. A bended specimen is shown in figure Figure 3.1 middle.



Figure 3.1: Cross cut test specimen (left), cylindrical mandrel bending test specimen (middle) and impact test testing apparatus (right).

Impact test

Additional information to the before mentioned tests can be gained from an impact test, described in chapter 1.3.2.3 and 5.3.3. It is testing the coatings resistance to shock like stresses. As for the bending test, a "fail-or-pass" test scenario was established with impact energies of 10, 25 and 49 mJ. Varnishes for industrial applications must meet higher standards but for a coating housed in a confined hull this is an appropriate range. Coatings already failing at 10 mJ should be considered not suitable for the application in adsorption heat transformation. This corresponds to the impact energy a 100 g object would have when dropped on the coated sheet from a height of 10 cm. Coatings failing at impact energies of 25 or 49 mJ can be considered suitable. Should the coating fail at impact energies above 49 mJ, the binder content can be possibly lowered to have more active mass in the coating.

Tape adhesion test

During the later stage of this work it was possible to test the adsorptive coatings using a tape adhesion test. Positive results could be obtained, the test is suitable for their characterization. This test allows gathering quantitative information such as adhesion forces as depicted in Figure 3.2. The adhesion force of this coating is 5 Nm and therefore quite low.



Figure 3.2: Tape adhesion test measurement - force needed for the detachment of a coating with a width of a 9 mm, moving average over 10 values.

3.1.1.2 Thermal stability

As stated in chapter 1.3.2.2 the thermal stability of the substances to be used is important for the later application. Thermogravimetric analysis, a proven method from the polymer industry was applied to characterize the thermal decomposition of the substances used. Onset points of

thermal weight loss was determined according to ISO 11358:1997 and used to identify substances that are applicable in adsorption transformation heat pumps, compare Figure 5.1. It is a valid measure for comparing degradation processes but it must be considered that an onset point of 400°C does not imply that the substance can be used up to 400°C. The difference between first weight loss and onset point, as well as the fact that kinetic effects make the degradation temperature appear higher than it would be in equilibrium conditions, demand that the weight loss onset point should lie well above the process temperatures.

Measurement of the complete coating including binder and adsorbent was considered for the assessment of the weight loss. In an open flow system like the one used here, the decomposition of the binder cannot be detected in this manner since desorption of the adsorbent and the corresponding weight loss cannot be distinguished from possible decomposition. An obvious approach would be to measure the coating – that is binder and adsorbent and then subtract the measurement of the adsorbent to correct for the desorption process. This was not possible. The presence of the binder changed the desorption kinetics of the adsorbent so that a correction yields false results.

In Figure 3.3, the according measurements are shown. The decomposition of pure binder is depicted in green. The typical curve arises from the measurement profile, compare chapter 5.4.1. Here with rising temperature the samples loses some weight. It continues to lose weight at 500°C where it is held for 30 min. this leads to the weight drop at T = 500 °C in the right part of the curve. The signal that is derived from a measurement of the coating with the measurement of the adsorbents desorption weight signal subtracted is depicted in red. For a better visual comparison the red signal was stretched along the y axis to match weight loss of the pure binder. The resulting signal is shown as "adjusted" in blue in Figure 3.3. What is important here is the course of the weight loss. It can be seen that, in the blue curve, desorption of the adsorbent was subtracted from this signal already. This shows that the binder investigated here changed the desorption process. The most reliable characterization of the decomposition process is therefore obtained by measuring the pure binder. It should be kept in mind that this does not allow for the detection of possible interactions of binder and adsorbent. These can be detected in cyclic stability tests comparing pure binder and binder adsorbent measurements.



Figure 3.3: Normalized weightloss of the pure binder and the binder in the coating calculated by substracting the adsorbents weightloss due to desorption from the overall coatings weightloss.

Some inorganic binders adsorb moisture which is then desorbed in the process of thermogravimetric analysis. Difficulties arising when trying to characterize such substances were solved by switching to more sophisticated measurement equipment. Here instead of a fixed heating rate the temperature is raised according to the weight loss. If a weight loss is detected, the temperature ramp is slowed down until the weight loss is over. Using this method, single decomposition steps could be resolved more accurately.

A less sophisticated but much faster method for determination of a substances weight loss is the use of a moisture analyzer. It consists of a balance and a heating element. While it does not provide a time resolved progression of the weight signal it still can be used to exclude substances with an early decomposition and free up measurement time of the thermogravimetric analysis. Alternatively, for additives, it can be used to proof that a substance will be cleared from the sample completely during curing.

For further insight into the decomposition process, temperature-controlled diffuse reflection FT-IR spectroscopy (T-DRIFTS) and in situ temperature controlled XRD measurements were applied to selected samples.

3.1.1.3 Porosity

The porosity of the coatings was characterized using the established methods nitrogen and water sorption. Nitrogen sorption was used to characterize the adsorbent pore structure. The measurement is fast and can be done as a standard test. Since results of nitrogen porosity 38

measurements cannot be quantitatively related to water adsorption the most promising samples have been further characterized by water sorption measurements.

3.1.2 Binder testing

Using the analytical methods established as described above, different binders have been characterized in regards to their thermal stability, change in porosity and mechanical stability. The results have been partly presented as an article in Industrial and Engeneering Chemistry Research and at various conferences.⁸³

3.1.2.1 Silicone binders

A selection of silicone binders has been investigated in regards to their applicability to adsorbent coatings in adsorption heat transformation adsorbers. For comparison, a polyester copolymer and an epoxy functionalized silicon oxide binder have been added to the investigation. A list of the binders together with the supplier, the chemical structure, the dispersion media and the curing conditions is given in Table 3-1. The dispersion media were chosen to be able to dissolve the binders, water based binders such as Silikophen® P40W or Silres® MP50 E were used as an emulsion of the polymer in water. In general a water based process is favored to a solvent based process for an industrial application because of less occupational health and safety concerns, lower disposal and environmental regulations and no explosion and fire hazards.

Curing at elevated temperatures was applied either to heat the presynthesized polymer chains above their glass transition temperature to initiate film formation or to provide the activation energy for crosslinking reactions. The binders curing with the help of a catalyst at room temperature such as Silikophen® AC1000 or Silres® MSE100 have the advantage of eliminating one production step. However, once the catalyst has been added, the slurry had to be processed in very short time. This is a disadvantage when using a dip coating process with a slurry bath that has a residence time exceeding the maximal processing time of the binder.

An ammonia exchanged Na-Y type adsorbent has been used in the investigation.

binder	supplier	substitution	dispersion media	curing	
Silikophen®	Evonik	nhanyl mathyl	water	250° C / 15 min	
P40W	L'VOIIIK	phenyi, menyi	water	250°C745 mm	
Silikopon® EW	Evonik	epoxy copol- ymer	xylene	250° C / 30 min	
Silikoftal®	Fyonik	polyester co-	acetone	250° C / 30 min	
HTS/MPA	LVOIIIK	polymer	accione	250°C750 mm	
Silres® REN 50	Wacker	phenyl, methyl	xylene	200° C / 60 min	
Silres® REN 60	Wacker	phenyl, methyl	xylene	200° C / 60 min	
Silres® HK46	Wacker	methyl	xylene	200° C / 60 min	
Silikophen®	E	phenyl, methyl	xylene: acetone =	2509 C / 15 min	
P80/MPA	Evonik		9:1 (w:w)	230° C / 43min	
Silikophen®	F:1 -		1	RT / cat I & II	
AC900	Evonik	phenyl, methyl	xylene	(0.75 %wt each)	
Silikophen®	F:1 -		1	DT / + U (2.0/)	
AC1000	Evonik	metnyi	xylene	RT / cat II (2 % wt)	
Silres®	W 71		1	DT / + U (2.0/)	
MSE100	wacker	methyl	xylene	KI / cat II (3 % Wt)	
Silres® MP50 E	Wacker	phenyl, methyl	water	200 °C / 240 min	
ESQUIM R-750	Esquim	phenyl, methyl	water	180 °C / 60 min	
G.1. W220	0.1.	epoxy funct.	water	180 °C / 15 min	
Silixan W220	Sılıxan	SiO2		cat III (1.2 %wt)	

 Table 3-1: List of binders, their chemical composition, dispersion media and curing temperatures used

cat I: tetra-n-butyl titanate and tetramethyl guanidine, cat II: tetra-n-butyl titanate, cat III: proprietary Silixan catalyst.

Silicone binders - porosity

Values for the BET surface area and pore volume derived from nitrogen sorption measurements of the resulting coatings are represented in Figure 3.4, the BET surface area and pore volume of pure adsorbent is depicted as the dashed top line at 1031 m²/g. Values for the coatings are listed in Table 3-2.

It can be seen that the highest pore volume of coatings, for binders like Silixan W220 or Silres® MP50 E, are about 70 % the pore volume of the pure adsorbent. Other binders like Silikopon® EW or Silikophen® P80/MPA showed a drastic decrease in pore volume down to 19 % of the pore volume of the pure adsorbent.

When taking into account that the pore volume is measured in regards to mass and that the coating incorporates a binder content of 15 %wt, the better performing binder show a fairly low decrease of the adsorbents pore volume. The binder has no porosity itself, so 15% reduction of the mass specific pore volume can be contributed to the presence of the binder. A sec-

ond dot-dashed line is drawn in Figure 3.4 at 85% of the pure adsorbent for visual comparison. Although all binder molecules used in this investigation are too large to enter the adsorbent micro pores it can be assumed that the binder decreases the accessibility of the pores. In the plot in Figure 3.5 the cumulative pore volume and its derivative are shown for a sample of a silicone binder with very low remaining pore volume, Silikophen® P40W, and one with high remaining pore value, Silres® MP50 E. There is an offset of 0.13 ml/g between the two curves in the left picture right from the start. This shows that most of the difference in pore volume can be related to pores smaller than the lower limit of this measurement which was 7 nm half pore width. In the right figure we can see that the difference in the pore accessibility between these two samples can be contributed mainly to pores with a half pore width of up to 50 nm. The difference is small for bigger pores. These inaccessible pores are blocked by the binder molecules. An intrusion of the polymer chain in the pore structure is not possible due to the size of the molecules. On the other hand the binder content is too low to block entire particles. A partially obstruction of the pore entrances by the binder is very likely but should not affect the accessibility that much. Measurement times are long enough to allow for intra particle diffusion which would restore the accessibility of the partially blocked particle. The exact mechanism of the binder blocking the adsorbent pores remains unclear, further discussion and experiments have been carried out by Kummer et al.⁸⁵ Nevertheless, a possible explanation why Silixan W220 and Silres® MP50 E are the best performing binders is that these polymers are prepolymerized large molecules that cannot block the pores as easily as the other smaller binder molecules. Consequently prepolymerized silicone binders can be assumed to achieve good pore accessibility when used in adsorbtive coatings.

binder	BET surface area	pore volume	p/po for pore volume	
	[m ² /g]	[cm ³ /g]		
Silikophen® P40W	404	0.17	0.99	
Silikopon® EW	226	0.12	0.99	
Silikoftal®	117	0.10	0.00	
HTS/MPA	44 /	0.19	0.99	
Silres® REN 50	279	0.18	0.99	
Silres® REN 60	343	0.20	0.99	
Silres® HK46	559	0.26	0.99	
Silikophen®	107	0.11	0.00	
P80/MPA	197	0.11	0.99	
Silikophen®	(17	0.25	0.00	
AC900	01/	0.23	0.99	
Silikophen®	(10	0.27	0.00	
AC1000	019	0.27	0.99	
Silres® MSE100	668	0.27	0.99	
Silres® MP50 E	739	0.30	0.99	
ESQUIM R-750	526	0.24	0.99	
Silixan W220	714	0.32	0.99	
CBV-300	1031	0.43	0.95	

 Table 3-2: BET surface area value, pore volume and the corresponding pressure.



Figure 3.4: BET surface area (red) and pore volume (turqouise) for the investigated coatings (columns) and the pure adsorbent (dashed line).



Figure 3.5: cumulative pore volume (left) and its derivative (right) for a slightly blocked Silres® MP50 E and a severely blocked Silikophen® P40W coating.

Results obtained for the measurement of BET surface area mirror those from pore volume. Here as well Silixan W220 and Silres® MP50 E were the best performing binders with a surface area of 714 and 739 m²/g remaining of the original 1031 m²/g for the pure adsorbent. This means that up to 72 % of the BET surface area remained. The worst performing binder Silikophen® P80/MPA showed a decrease to only 197 m^2/g or 19 % of the original surface area.

BET surface area values allow for a comparison to recent work found in Literature. Li et al. report BET surface areas for adsorbent coatings, the best performing coating was 10 % corn starch binder in a silica gel coating. Here the BET surface area decreased to 58 % of its original value. Compared to these results the binders investigated here are performing exceptionally well. They achieve a better pore accessibility even with the higher amount of binder content.

Drawing an overall conclusion we can state that, out of the investigated binders, there are several ones that did not obstruct the adsorbents porosity. They can be used for coatings in heat transformation applications. For the most promising one, Silres® MP50 E, a water sorption isotherm has been measured to ensure that the result obtained for nitrogen sorption measurements is valid for water sorption as well. The isotherm is depicted in Figure 3.6 together with the water isotherm of the pure adsorbent. While the offset between the curves can be attributed to the 15 % non-porous binder in the coating the slight spread of the isotherms at higher pressures is a sign for minor influence of the binder on the coatings sorption characteristics. Also desorption is slower for the coating resulting in the slight hysteresis between adaddesorption due to kinetic effects.



Figure 3.6: Water isotherms of Silres® MP50E coating and the pure adsorbent.

Silicone binders - thermal stability

Characterization of the binders thermal stability has been carried out using thermogravimetric analysis on all of the binders. A weight loss of the binder sample shows degradation of the binder at that temperature. The gaseous degradation products would interfere with the sorption process, compare chapter 1.3.2.2. The resulting weight loss curves are depicted in Figure 3.7, and the onset points for thermal weight loss are given in Table 3-3. For samples that showed two distinctive weight loss onsets, both temperatures are listed in the table. The range of weight loss was large, weight losses from only 3 % for the HK46 binder and weight losses of up to 78 % for the P40W binder were observed. Onset temperatures ranged from 67 °C for the Silixan W220 binder up to 444 °C for the Silres® REN 60 binder.

binder	onset	2 nd onset
	[°C]	[°C]
Silikophen® P40W	393	
Silikopon® EW	394	
Silikoftal® HTS/MPA	94	361
Silres® REN 50	433	
Silres® REN 60	444	
Silres® HK46	206	
Silikophen® P80/MPA	411	
Silikophen® AC900	95	388
Silikophen® AC1000	79	
Silres® MSE100	84	
Silres [®] MP50E	410	
ESQUIM R-750	*	
Silixan W220	67	276

Table 3-3 : Onset temperatures for weight loss during TGA

*Due to excessive gas formation and foaming upon heating, the ESQUIM R-750 could not be characterized.

44



Figure 3.7: Thermogravimetric analysis of the different silcone binders – weight loss as a function of temperature.

Five binders show a weight loss at distinctively lower temperatures, even below 100°C - Silikoftal® HTS/MPA, Silikophen® AC900, Silikophen® AC1000, Silres® MSE100 and Silixan W220. Silikoftal® HTS/MPA is a polyester copolymer type binder. Its early decomposition can be attributed to its chemical nature. The other four binders are catalytic hardening binders that cure at room temperature (Silikophen® AC900, Silikophen® AC1000, Silres® MSE100) or for a very short time at slightly raised temperatures (Silixan W220, 180 °C, 15 min). A possible assumption would be that because of the missing high temperature curing step the solvents used for the coating could not be removed entirely. To avoid interference like these all samples have been conditioned before the measurement in a stream of dry nitrogen at 40°C for 60 min to remove residual volatile substances. A straightforward approach to avoid the early weight loss of these binders would be a high temperature drying step or reduced pressure to evaporate the residual solvents. For the Silikophen® AC900 binder it could be exemplary shown, that such a drying step eliminated its low weight loss onset. Another explanation although less likely is the following: no solvents were removed but a decomposition step took place during the temperature treatment step. The decomposition was carried out completely during this step but the remaining substance starts another decomposition step at higher temperatures.

Although this temperature treatment steps is partially solving the problem of these binders lack of thermal stability it would lead to the same amount of process steps as the temperature curing binders. Additionally though, the drawbacks of room temperature drying binders, like short can-times are still remaining.

Further investigations on the weight loss of the room temperature curing binders were carried out using T-DRIFTS. In this analytical method IR spectra were continuously recorded in situ while the temperature was raised. The according measurements are depicted in Figure 3.8, Figure 3.9 and Figure 3.10. The absolute absorbance values cannot be compared in between these measurements but the declining absorbance with rising temperature shows qualitativley that a reaction is taking place. The area of interest here is emphasized by a blue rectangle. Here, all of the binders showed a broad loss of intensity at 3500 cm⁻¹ during the heating process. This wavelength is characteristic for the IR-absorbance of hydroxyl groups. The loss can therefore be contributed to a decline in the number of hydroxyl groups. The hydroxyl- and or alkoxy groups undergo a condensation reaction and silicon-oxygen bonds are formed while the corresponding water or alcohol is generated as a byproduct, as explained in chapter 1.3.1 and figure Figure 1.7. The binder in the samples investigated here had not completely cross-linked at room temperature and now, under elevated temperatures this crosslinking is completed.

The early weight loss of these binders can therefore be contributed to the loss of water in this crosslinking reaction. Stoichiometric considerations were used to check whether it is possible, that the whole weight loss stems from this reaction. According to the supplier Wacker the complete weight loss by the crosslinking reaction is about 30 %wt for Silres® MSE100. The weight loss observed here for the additional crosslinking at elevated temperatures was 8 %wt. For Silikophen® AC900 the share of methoxy groups of the complete molecular weight is 17 %wt. Complete hydrolyzation would result in 10 %wt of hydroxyl groups. This corresponds to a hypothetical weight loss of 5 %wt due to condensation of hydroxyl groups, compare Figure 1.7 . In conclusion a weight loss for the measured binders should be lower since methoxy groups are hydrolyzed by the curing reaction that has already partly taken place in the coating. AC900 lost 5 %wt of its mass in the first decomposition step. The same calculation gave a theoretical weight loss from 12 %wt to 35 %wt for Silikophen® AC1000. The observed weight loss here was 8%wt. In conclusion the weight loss of these binders can be contributed to a not entirely completed crosslinking reaction at low temperatures.



Figure 3.8: T-DRIFTS measurement of the Silres® MSE100 binder, IR Spectra on the y axis, intensity is color coded.



Figure 3.9: T-Drift measurement of the Silikophen® AC900 binder, IR Spectra on the y axis, intensity is color coded.



Figure 3.10: T-DRIFTS measurement of the Silikophen® AC1000, IR Spectra on the y axis, intensity is color coded.

Silicone binders - mechanical testing

Cross cut test, bending test and impact test have been performed on all coatings. Results are given in Figure 3.11 and Table 3-4. For a better graphical comparison the results were converted into a test score ranging from 3 for the best possible to 0 for the worst result. Details of the scoring system are described in chapter 5.3 in the experimental section.

binder	cross cut test	failure mode adhesion/ cohe- sion	bending test failing diameter	impact test fail- ing energy
<u>a''''</u>	[GK]		[mm]	[mJ]
Sılıkophen®	2	a	32	25
P40W				
Silikopon® EW	2	a/c	16	25
Silikoftal®	2		16	25
HTS/MPA	3	С	16	25
Silres® REN 50	2	с	4	49
Silres® REN 60	3	с	4	10
Silres® HK46	2	a	16	25
Silikophen®	2		16	10
P80/MPA	3	C	10	10
Silikophen®	1		16	25
AC900	1	С	10	23
Silikophen®	1	2	16	40
AC1000	1	C	10	49
Silres® MSE100	1	с	16	25
Silres® MP50 E	4	с	32	25
ESQUIM R-750	5	с	16	49
Silixan W220	4	а	16	25

Table 3-4: Results of the mechanical testing - cross cut rating and the corresponding failure mode, failing diameters for the bending test and failing impact energies for the impact test.



3

Figure 3.11: Comparison of the mechanical stability of coatings with different binders, bending test (black), cross cut test (turquoise) and impact test (red).

In the cross cut test the best performing coatings were those with Silikophen® AC900, Silikophen® AC1000 and Silres® MSE100 binders. The ESQUIM R-750 binder coatings showed the poorest performance. The test results obtained covers nearly the whole range of possible results from GK 0 to GK5. Therefore the cross cut test is well suited to characterize the coatings. Additionally, since it is used by other researchers working on adsorptive coatings it allows for comparison with literature.^{12,33,113} Results in other works correspond to a cross-cut rating of GK 3 for silane-zeolite composite coatings using N-propyl-trimethoxysilane and a range from cross-cut rating GK 1 to GK 3 was achieved for coatings up to 15 µm using various silanes with different substitutions. When comparing these results it has to be kept in mind that thinner coatings in general show better results in the cross cut tests.

The coatings failure mode was determined and is listed in the second column of Table 3-4. Examples for an adhesion and cohesion failure were given in Figure 1.8. Most coatings show a cohesion failure like the Silres® MSE100 based coating. Only three coatings showed adhesion failures, for example the Silixan W220. The prominence of cohesion failures is a result of the adaption of the coating to a low binder content to maximize the fill factor in a later application in an adsorber. As explained in chapter 1.3.2.3, these results could be improved, by raising the binder content but the active mass on the adsorber will then decrease. Nonetheless, the results show that most coatings are stable enough for the modest requirements concerning mechanical stability in adsorptive heat transformation adsorbers. Higher binder content is not necessary for most binders. A severe inhomogeneity of the binder by settling can be ruled out since this leads to peeling off of the coating during curing. A minor inhomogeneity is likely

and normal. Concerning investigations have been carried out by Schabel in the project "MAKSORE".

In the bending test only the Silres® REN 50 and Silres® REN 60 showed a good resistance. All others performed rather poorly. Altogether the coatings showed just a limited stability during the bending test compared to conventional coatings that often that resist mandrel diameters of 2 mm.^{114,115} This is not surprising, as in the cross cut test the low binder content plays a role and the thickness of the coating was ~175 μ m, and therefore much thicker than in a conventional coating application. Thicker coatings are generally mechanically less stable. The coatings can still be considered suitable for the application in adsorption heat transformation since the bending stress experienced in the lifetime and production of an adsorber is minimal unless a coil coating process is used for the production.

The impact test shows similar results to the cross cut test. Only ESQUIM R-750 has fairly strong resistance to the deformation experienced during the impact test while showing very bad results in the cross cut test. A possible explanation would be that the adhesion of the coating itself is quite flexible and only it's adhesion to the metal surface is poor. This can be ruled out because the failure mode of the ESQUIM –R-750 coating is typical for a cohesion failure, see Figure 3.12.



Figure 3.12: Cohesion failure of the ESQUIM R-750 binder.

Drawing an overall conclusion, out of the tested silicone binders the Silres® MP50 E showed the best performance. Allthough it did not achieve the highest results in every single category its good overall performance together with its water-based formulation made the most suited binder for further research.

3.1.2.2 Inorganic binders:

A higher driving temperature allows for a more efficient process using more ambient heat. Some engineering problems have to be solved to implement a process with higher desorption temperatures. One of these problems is to fabricate coatings that can withstand higher temperatures up to 400°C. Although some silicone binder are marketed as stable up to 600°C this only holds true in special formulations with large amounts of dedicated fillers. These formulations are not applicable to adsorptive coatings in heat transformation applications and the formulations used so far do not withstand temperatures of 500 °C, see Figure 3.13. To address

3

this matter a variety of inorganic binders have been investigated. Their thermal stability exceeds that of organic binders by far, use cases with temperatures exceeding 1000 °C are common in industrial applications. Nevertheless they must meet the special requirements of adsorption heat transformation technology.



Figure 3.13: Silres® MP50 E based coating after tempering at 500 °C for 300 min.

The investigated inorganic binders are shown in Table 3-5 together with their curing conditions and chemical compositions. Resbond 794, HPC-Binder and Apyral 180E had been selected initially but have been dropped from the test because no suitable coatings could be achieved with the binder content of 15 %wt - the coatings would crack instantly when handling the samples. The first four binders, Sivo 140, Silres® REN 50, Silres® REN 60 and Silres® HK 46, are initially silicone binders that have the possibility to be cured to silicone oxide, compare Figure 3.14. During this process the organic constituents are oxidized to carbon dioxide and water. Silicone oxide is formed that acts as a binding agent between the adsorbent particles, see Figure 3.14. Sasol Disperal P2 consists of aluminum hydroxide particles usually used for microcrystalline aluminum oxide ceramics. The particles are dispersed in the coating slurry and form aluminum oxide by dehydration during the curing process Temperatures of 250 °C or more are needed for the transformation to aluminum oxide. Nevertheless the Sasol Disperal P2 Binder was used as recommended by the supplier and cured at room temperature. Possibly the binder acts as a binding agent at lower temperatures as well and is intended to cure during its use at elevated temperatures. To confirm this assumption and rule out other effects the binder was investigated using temperature resolved X-Ray diffraction measurements a technique available in-house at Fraunhofer ISE, see Figure 3.15. Up to 200 °C no change in the X-ray diffraction pattern is observed, hence no structural change takes place - this is consistent with literature according to which the phase change from bohemite to gamma aluminum oxide takes place at temperatures above 400 °C.¹¹⁶

The LRC binder chemically consists of aluminum oxy nitrate hydrate that cures to an aluminate losing NO_x and water in the process. The Ceramabind 644-S binder consists of colloidal silica particles that dehydrate and sinter to form a continuous solid.

Binder	Curing	Chemical compostition
Sivo 140	1 h 200 °C, 4 h 350 °C	silane, cured to SiO ₂
Silres® Ren 50	1 h 200 °C, 4 h 350 °C	silicone, cured to SiO ₂
Silres® Ren 60	1 h 200 °C, 4 h 350 °C	silicone, cured to SiO ₂
Silres® HK 46	1 h 200 °C, 4 h 350 °C	silicone, cured to SiO ₂
Sagal Dignaral D2	рт	aluminiumoxide hydroxide,
Sasoi Disperal P2	K1	boehmite
potassium silicate	RT	silicate
Resbond 792	2 h 120 °C	silicate
Resbond 793	2 h 120 °C	silicate
Resbond 795	2 h 90 °C, 2 h 315 °C	aluminate
LRC Binder	24 h RT, 1 h 200 °C, 2 h 350 °C	aluminate
Ceramabind 644-S	RT, 2 h to 90 °C, 2 h to 150 °C, 2	
	h 150 °C	conoidal sinca

Table 3-5: List of binders, their curing temperatures and chemical composition.

 $[SiO(CH_3)_2]_n + 5n O_2 \rightarrow n SiO_2 + 2n CO_2 + 3n H_2O$

Figure 3.14: Silicone resin reacting to silicon oxide.



Figure 3.15: In situ temperature dependend X-ray diffraction pattern of Disperal P2 (shifteted by 10 a.u. for better comparisson). No structural change took place during the temperature treatment up to 200 °C.

Inorganic binders - porosity

Nitrogen measurements have been performed on the coatings obtained with the inorganic binders. Results are shown in Table 3-6 and Figure 3.16. The highest remaining pore volume was measured for the silicate binders Resbond 793 and Resbond 792 with 83 % and 82 % of the pure adsorbents pore volume remaining. The most degradation in pore volume was observed for the Silres® HK46 binder, the remaining pore volume is only 43 %. The binder was tested as a silicone binder without pyrolysis in the silicone binder test series in chapter 3.1.2.1. Here a remaining pore volume. This effect could not be observed for Silres® Ren 50 and REN 60, the other two silicone binders that can be cured to yield silicone dioxide. Here the pore volume with pyrolysis is larger than without. In general the loss of pore volume for inorganic binders is in the acceptable range with many coatings having 60 % to 70 % of their initial pore volume remaining. However, all pore volume and thus water uptake ability that is lost in the coating process must be replaced by incorporating more adsorbent in the fabrication process of the adsorber.

The BET surface measurements shows similar results, the highest BET surface area was measured for the Resbond 792 binder coating, the lowest remaining surface was measured for the HK46 binder coating. In general it can be stated that coatings with an intact porosity can be fabricated using inorganic binders like Resbond 792 and 793.

binder	BET surface area	pore volume	p/p0 for pore volume
	[m ² /g]	[cm ³ /g]	
Sivo 140	732	0.295	0.952
Silres® Ren 50	605	0.257	0.990
Silres® Ren 60	583	0.299	0.989
Silres® HK 46	478	0.181	0.950
Sasol Disperal P2	700	0.319	0.901
potassium silicate	733	0.310	0.950
Resbond 792	814	0.353	0.899
Resbond 793	713	0.358	0.990
Resbond 795	600	0.261	0.951
LRC Binder	714	0.299	0.949
Ceramabind 644-S	569	0.282	0.900
CBV-300	1031	0.431	0.949

Table 3-6: BET surface area,	pore volume and the corresp	onding pressure for the coat-
	ings with inorganic binders	



Figure 3.16: graphical representation of the remaining pore volume and BET surface area of the coatings with inorganic binders.

Inorganic binders - thermal stability

TGA has been performed on the cured binders, see Table 3-7 and Figure 3.17 It was expected that there is no substantial weight loss for the inorganic type binders, especially the metal oxide type binders. Surprisingly, many of these binders showed an early weight loss. For the silane and silicone binders this can be contributed to an incomplete decomposition of their organic constituents in the curing step. Sivo 140 and Silres® HK46 show an early weight loss onset at below 100°C. High resolution measurement have been carried out, they show two distinct weight loss steps at 57 °C and 389 °C for SIVO 140 and at 62 °C and 261 °C for HK46. A complete removal of the degrading substances in a further process step is unlikely to yield better results since curing at 350 °C for 4 h was not sufficient for their removal. Both binders are therefore classified as unsuitable for coating in a reduced pressure environment at high temperatures like in gas adsorption heat pumps. The Silres® Ren 50 and Ren 60 Binders on the other hand have a relatively high onset temperature at above 450 °C and can be considered suitable for the application in high temperature applications from a thermal stability point of view. Disperal P2, with its high weight loss onset can be considered suitable for high heat applications, too. The weight loss can be partially contributed due to the phase change from bohemite to gamma aluminum oxide. In this process only water is generated as a byproduct which would not harm an adsorption process with water as adsorptive. Two moles of bohemite react to form one mole of aluminium oxide and one mole of water. With the molar masses of bohemite (60 g/mol), aluminum oxide (102 g/mol) and water (18 g/mol) the weight loss during the reaction can be calculated to be 15 %wt. The weight loss measured here was 20 %wt. Hence another process must be present – most likely the binder is partially hydrated and then loses that water in the process. The early weight loss of the potassium silicate binders is most likely related to its incomplete curing at room temperature. Surprisingly the Resbond Series binders from the material class of silicates (792 and 793) and aluminates (795) show very low weight loss onset temperatures, for 793 and 795 even below their curing temperatures, compare Table 3-7.

Binder	1 st Onset [°C]	2 nd Onset [°C]
Sivo 140	69	-
Silres [®] Ren 50	484	-
Silres® Ren 60	488	-
Silres® HK 46	75	-
Disperal P2	40	-
potassium silicate	122	-
792	131	419
793	88	-
795	40	-
LRC	58	388
644-S	78	-

Table 3-7: Thermogravimetric analysis onset temperatures for the inorganic binders



Figure 3.17: Thermogravimetric analysis of the different inorganic binders – weight loss as a function of temperature.

Information on the exact curing mechanisms could not be obtained from the supplier. Owing to these low weight loss temperatures the binders were therefore classified as unsuitable. The LRC binder showed an early weight loss followed by a weight loss at higher temperatures. It showed an total loss off 23 % wt and the weight loss was not taking place at one single early step but occured continuously over the full range of the temperature spectrum. Standard TGA measurements and high resolution measurements showed consistent results. Here the loss of NO_x that was generated in the curing step might have played a role. According to the manufacturer this process only starts at around 500 °C. T-DRIFT measurements have been carried out to confirm whether this early weight loss can indeed be traced back to a loss of NO_x, compare Figure 3.18. A clear peak at 1375 cm⁻¹ can be observed in the low temperature spectra that loses intensity with rising temperature. While the peak cannot be assigned to a NO₃ or NO_x group with certainty, it is clearly visible that the process continues up to temperatures well above 600°C. It can be assumed that with curing at temperatures of above 700°C it is possible to completely remove the substance. These temperatures would be very challenging to the adsorbent and heat exchanger materials and are not likely to be used in a production process of adsorbers in the future. The binder is therefore considered not suitable for the use in adsorbers for heat transformation applications.



Figure 3.18: T-DRIFT measurements of the LRC binder at different temperatures.

For the Ceramabind 644-S binder the quantitative weight loss of only 2 %wt was rather small, it occured at low temperatures. It can be contributed to water lost in the sintering process of the colloidal silica particles.

Summarizing it can be said that the best thermal stability was shown by the cured silicone binders Silres® REN 50 and REN 60 and the Disperal P2 binder. With a fine tuning of the curing process to the requirements of adsorption heat transformation systems some of the other binders could be used at temperatures of 500°C. To ensure good thermal stability, attention has to be payed to the curing process. Longer curing times, higher temperatures, reduced pressure or a combination thereof will yield the best results. This translates to a higher production costs and higher stress on the adsorbent and heat exchanger material. An analytical approach would be to use TGA-GC-MS coupling to investigate the chemistry of the substances lost. If only water is lost the binder can be used safely for water based processes. Especially Ceramabind 644-S and Disperal P2 are likely to lose only water.

Inorganic binders - mechanical stability

The mechanical stability of the obtained coatings has been characterized using cross cut, bending and impact tests. The results are presented in Table 3-8. The overall picture is clear - the inorganic coatings show a very poor performance in the mechanical tests. In the results of the cross cut test only the two highest and therefore worst possible values were found. A value of GK 4 corresponds to a coating detachment between 35 % and 65 % of the sample area, a value of GK 5 to a detachment of more than 65 %.

The mandrel bending test shows even more instability - all coatings failed at the lowest possible value. In the impact test the resistance is in the average range for all binders. Regarding

the mechanical stability, none of the coatings can be considered stable enough to be used in the intended application. This is especially true when considering that thermal and thus mechanical stresses will increase compared to normal temperature conditions. Adhesion could possibly be improved by a suitable pretreatment method. Commonly used adhesion promoting layers are organic coatings and will most likely not withstand the temperatures encountered. Mechanical pretreatment and surface morphology modification could be a possible route for better adhesion. Another way, patented by Dawoud et al. could be to use fiber reinforcement in the coating.⁷⁹ Suitable fibers could improve mechanical stability and thermal conductivity in the coating simultaneously. Nevertheless fibers would not improve adhesion problems and the content of active material per volume would be reduced. A medium sized, full scale heat exchanger was coated as a test object. The peeling off of the coating could be observed at several spots without any intentional mechanical or thermal stresses on the adsorber other than those that arise during handling.

failure mode, failing diameters for the bending test and failing impact energies for the				
impact test.				
binder	cross cut test	failure mode adhesion/ cohe-	bending test failing diameter	impact test fail- ing energy

Table 3-8: Results of the mechanical testing - cross cut rating and the corresponding

Sinder	test	adhesion/ cohe- sion	failing diameter	ing energy
	[GK]		[mm]	[mJ]
Sivo 140	5	С	32	25
Silres® REN 50	4	a	32	25
Silres® REN 60	4	a	32	25
Silres® HK46	5	a	32	25
Disperal P2	4	С	32	25
potassium sili- cate	5	a	32	50
792	5	a	32	25
793	4	С	32	25
795	4	С	32	25
LRC	5	a	32	25
644-S	4	a	32	25

Concluding the test on inorganic binders it can be stated that the porosity of the resulting coating is not severely compromised and some well performing binders could be identified. Some of the better performing binders show a decent thermal stability - Disperal P2 seems to be the best compromise between high remaining porosity and good thermal stability. None of the coatings investigated showed sufficient mechanical stability to be used as such without further modification.

3.2 Optimization of metal-to-adsorbent mass ratio

3.2.1 Motivation

During preliminary works a heat exchanger was coated with TiAPSO adsorbent and its power output characterized in a large temperature jump test. In an experiment on the suitability of rheology additives for the use in full scale adsorbers another heat exchanger of the same model was coated with a higher amount of TiAPSO adsorbent, see Table 3-9.

Quantity	unit	HX-A – thinner coating	HX-B – thicker coating
dimensions	mm ³	$300 \times 49.5 \times 121$	$300 \times 49.5 \times 121$
volume coatable structure	L	0.98	0.98
volume complete HX	L	1.80	1.80
mass HX	kg	1.11	1.12
mass adsorbent	g	117	330
mass ratio	kg_{HX}/kg_{S}	9.5	3.4
fill factor	$kg_S/m^3_{\rm HX}$	65	181
picture of coated adsorber			

	Table 3-9:	Coated	heat	exchangers	and t	their	proj	perties.
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It is well known from literature, that an increase of adsorbent mass on the same heat exchanger er results in a higher coefficient of performance (COP) because of the better mass ratio between heat exchanger and adsorbent. At the same time the power decreases because of the slower mass and heat transfer through the coating layer. Strikingly, for the pair of adsorbers described above, the measurements showed a different trend. Even though the thicker coating took longer to complete the adsorption half cycle, $t_{90,HX-B} = 253$ s compared to $t_{90,HX-A} = 178$ s, the power output is higher for the thicker coating. HX-B has 2.8 times more adsorbent mass and thus more energy output in the time that is longer by a factor of 1.4. The thinner coated adsorber achieved a mean power of $P_{HX-A} = 514$ W, the thicker a power of $P_{HX-B} = 838$ W. The power output of the two adsorbers is shown in Figure 3.19. The rheology additive could be ruled out as the reason for this effect by small scale sample measurements.



Figure 3.19: Power output of the two identical adsorbers with different amounts of coatings.

These findings are extremely interesting. If the effects which lead to these counter intuitive results could be reproduced, understood and applied to other adsorbers it would be possible to raise the adsorbers energy efficiency by using more adsorbent without sacrificing the adsorbents power. As Wittstadt et al. state "a main focus of R&D on adsorption modules for thermally driven heat pumps and chillers has been to enhance the volume specific power output while maintaining a reasonable coefficient of performance".¹¹⁰ To gain a deeper understanding about the underlying causes several experiments were carried out. Small scale samples were coated in 4 different thicknesses and tested in the kinetic testing rig. In parallel, 5 identical heat exchangers were coated with varying amounts of adsorbent and their performance analyzed using the ADSEL test rig available at the Fraunhofer ISE.

3.2.2 Coating of the samples

3.2.2.1 Small scale samples

Four small scale samples were prepared, their coatings layer thickness ranged from 165 to $470 \,\mu\text{m}$, see Table 3-10. An aluminum sheet was used as substrate. The samples were coated with TiAPSO as adsorbent and Silres® MP50E silicone binder. The coating thickness was achieved by layering several coating layers on top of each other in consecutive dip coating steps. This led to variations in the coating thickness. Nevertheless the samples were considered suitable models of the full scale adsorbers. These have a variation of coating thickness as well due to edges and notches where the slurry accumulates, see Figure 3.20. The samples properties are given in Table 3-10.

quantity	unit	SSc-1	SSc-2	SSc-3	SSc-4	
thickness	[µm]	165	212	312	470	
standard deviation	[µm]	40	24	89	80	
adsorbent mass	[mg]	237	328	454	624	
max. water uptake	[mg]	76	105	145	200	

 Table 3-10: Properties of the coated small scale samples

3.2.2.2 Heat exchangers

Five identical heat exchangers were coated with the same coating as the small scale samples above using TiAPSO and Silres® MP50E. Aluminum fin flat tube heat exchangers were used. The heat exchanger properties are listed in Table 3-11, the heat exchangers are depicted in Figure 3.20.

Quantity	Unit	HX 1 - 5
total metal mass	kg	0.465
material	-	aluminium
volume	L	1.43
tube height	mm	1.79
tube width	mm	16.35
fin height	mm	8.15
fin thickness	mm	0.80
fin pitch	mm	2.36

Table 3-11: Properties of the heat exchangers coated

The heat exchangers were coated with different amounts of adsorbent. Adsorbent masses that were deposited on the heat exchangers ranged from $m_{s,HX-1} = 62$ g for HX-1 up to $m_{s,HX-5}543$ g for HX-5, see Table 3-12. During the dipcoating process the amount of slurry applied in each coating phase increased substantially making control of the final weight difficult. The coating thickness increases and the size of the gas access channels decreased from HX-1 to HX-5. All lamellas were homogeneously coated with adsorbent; the edges and corner were completely coated, see Figure 3.20. The coating thickness increased considerably at the flat tubes lateral surfaces because the slurry cannot be blown off as effectively here as at the lamellas. At the flat tubes the adsorption heat can be dissipated effectively into the cooling fluid thus making the increased thickness beneficial for a fast ad- and desorption process. When comparing the adsorbent mass of these adsorbers coated here to others in literature a specific quantity must be used. The fill-factor relates the adsorbent mass to the heat exchangers volume. It is a useful quantity for considerations of construction volume during layout of adsorber modules. Fill factors achieved for the adsorbers coated here ranged from φ_{HX} .
$_1 = 44 \text{ kg}/\text{m}^3$ up to $\varphi_{\text{HX-5}} = 382 \text{ kg}/\text{m}^3$. In literature values from 116 kg/mmm to 226 kg/mmmm kg/mmmm kg/mmmm kg/mmmm kg/mmmm kg/mmmmm kg/mmmmmm kg/mmmmmm kg/mmmmmm kg/mmmmm kg/mmmmm kg/mmmmm kg/mmmmm kg/mmmmm kg/mmmmm kg/mmmmmm kg/mmmmm kg/mmmm kg/mmm kg/mmm kg/mmmm kg/mmmm kg/mmm kg/mmm kg/mmm kg/mmmm kg/mmmm kg/mmm kg/mmmm kg/mmm k

Another useful specific quantity is the heat exchanger mass ratio. It relates the adsorbent mass to the heat exchanger mass. It is of importance since the heat exchanger has to be cooled down and heated up in every adsorption cycle which makes small metal to adsorbent ratios more desirable. Adsorber mass ratios ranged from $r_{HX-1/S} = 7.42 \text{ kg}_{HX}/\text{kg}_S$ to $r_{HX-5/S} = 0.85 \text{ kg}_{HX}/\text{kg}_S$. In general, the lower the mass ratio is, the better the COP will be for a given adsorbent metal combination. For a better comparison to literature data these values are neglecting the binder content. When taking into account the binder and considering it as part of the inert heat exchanger mass, the mass-ratios change to $r_{HX-1-B/S} = 7.62 \text{ kg}_{HX}/\text{kg}_S$ and $r_{HX-5+B/S} = 1.03 \text{ kg}_{HX}/\text{kg}_S$. In a simulative approach the masses have to be weighed by their respective heat capacities and the heat capacity of the adsorbent itself has to be taken into account.

Quantity	Unit	HX-1	HX-2	HX-3	HX-4	HX-5
sorbent mass	[g]	62	195	301	445	543
mass ratio	[kg _{HX} /kg _S]	7.42	2.37	1.54	1.04	0.85
fill factor	$[kg_s/m^3]$	44	138	212	313	382

Table 3-12: Sorbent mass, mass ratio and fill factor of the coated adsorbers



Figure 3.20: HX-1 to HX-5 from left to right.

Several groups have presented full scale coated heat exchangers in literature, nevertheless the mass ratio is rarely reported or can be deduced from the information given.^{24,26,37,112,118} Cordierite monoliths coated with zeolite for the use in catalysis applications by Zamaro et al. reached a mass ratio of $r_{HX/S} = 8.33 \text{ kg}_{HX}/\text{kg}_S$ and $r_{HX/S} = 6.67 \text{ kg}_{HX}/\text{kg}_S$.¹¹⁹ Dawoud et al. and Freni et al. coated metal heat exchangers with mass ratios from $r_{HX/S} = 4.35 \text{ kg}_{HX}/\text{kg}_S$ to $r_{HX/S} = 2.22 \text{ kg}_{HX}/\text{kg}_S$.^{77,117} Wittstatt et al. presented results of an adsorber with directly crystalized SAPO-34 that had a mass ratio of $r_{HX/S} = 2.63 \text{ kg}_{HX}/\text{kg}_S$.¹¹⁰

The heat exchangers presented here exceed the mass ratios of heat exchangers presented in literature so far. Mass ratios cannot only be influenced by the coating process but by the adsorber design as well. Tailor-made heat exchangers for adsorption heat transformation might yield even better mass ratios and could be optimized for an efficient adsorption process. At

this stage of the development of adsorption heat pumps the number of heat exchangers produced would be very low. From an economic point of view this would make such a custom made heat exchanger fairly expensive compared to off the shelf heat exchangers produced for mass markets like automotive cooling with their cost optimized production processes.

3.2.3 Characterization

3.2.3.1 Small scale samples

The small scale samples were characterized using three different types of measurements – large pressure jump adsorption measurements, large temperature jump adsorption measurements and large temperature jump desorption measurements. Large temperature jump measurements are more closely simulating the process that takes place in the adsorption heat pump, while large pressure jump measurements are more comparable to the ADSEL-Test measurements performed on the full scale heat exchangers.

Large pressure jump measurements

Large pressure jump measurements have been carried out on all of the four small scale samples. During the measurement the loading of the adsorbent increased as a result of the water vapor pressure step function applied. This is recorded by the pressure sensors in the measurement chamber, see chapter 5.9 for details.

The course of the decreasing pressure during the measurement is depicted in Figure 3.21. All samples start at same pressure consequently the initial loading is equal for all the samples. The different final pressure at the end of the measurements is a consequence of the different amounts of adsorbents on the samples. These adsorb different amounts of water from a constant volume of gas that initially contained the same amount of water vapor. Looking closer at the decreasing part of the curve, it can be seen that there was an initial steep drop, then a sustained linear pressure drop which in the end flattened out once the pressure approached its equilibrium state. In the linear part of the measurement the drop of the pressure seems similar for all four samples. Here, between 10.1 and 20.5 s the measurement can be approximated by a linear fit which gave the slopes for the 4 samples that are shown in Table 3-13. The speed of the dropping pressure increased from SSc-1 to SSc-3.

l'abl	e 3-13:	Slope of	the decreasing	g pressure in	the first	part of t	he measurement
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Sample	unit	fitted slope
SSc-1	[Pa s ⁻¹]	-12.9
SSc-2	[Pa s ⁻¹]	-15.5
SSc-3	[Pa s ⁻¹]	-17.9
SSc-4	[Pa s ⁻¹]	-14.4

The thicker coating on SSc-4 was slightly slower in adsorbing the water vapor than the thinner ones. This can be a result of the slower heat transfer for the thicker coating layer heating up the coating. The higher temperature is then shifting the equilibrium conditions and thus lowering the driving force. Consulting the maximum surface temperatures in the measurement, plotted in Figure 3.22, this assumption can be confirmed. Maximum surface temperatures measured ranged from 55.0 °C for SSC-1, the thinner coating, to 59.8 °C for SSC-4, the thicker coating. The surface temperature of the thicker coating was constantly higher.



Figure 3.21: Decreasing pressure during adsorption for a LPJ measurement of the small scale samples.



Figure 3.22: Course of surface temperature for SSc-1, the thinnest and SSc-4, the thickest small scale sample during a LPJ measurement.

The power output is a linear function of the time derivative of the dropping pressure for these samples. The higher amount of adsorbent in the thicker coatings allowed them to adsorb more water per time as the thinner coating. This leads to the hypothesis that mass transfer in the coating seems not to be the limiting factor in this process. Otherwise the thicker coatings could not adsorb water vapor at a similar rate as the thin one and the pressure drop would be slower for thicker coatings.

The time needed to advance from 0 % to 90 % of the final loading (t₉₀), the loading at t₉₀ (X₉₀) and the mean adsorption power over the adsorption time (P) were calculated (see chapter 5.9 for details) as well as the logarithmic mean temperature difference (Δ T) between the equilibrium temperature of the adsorbent and the cold plate temperature. This is the driving temperature differences, see chapter 1.4.2. The corresponding values are given in Table 3-14.

The t₉₀-time is related to the adsorbent mass on the sample. It increases from 10.5 s for the thinnest coating to 60 s for the thickest coating. The mean power output delivered by the samples decreased considerably by a factor of two from 14.3 W for the thin to 7.0 W for the thicker coating. This can be partly contributed to the higher driving forces available to the process. The UA value relates the delivered power to the driving temperature difference available to the process and is calculated as their ratio. When calculating the UA value for the samples, it decreases from 0.7 W/K for SSC-1 to 0.4 W/K for SSC-4. If one assumes, that the whole adsorption process was only limited by the heat transfer from the adsorbent to the aluminum sample plate the corresponding heat transfer coefficient $\alpha = UA/A$ can be calculated using the samples area of A = 1480 mm², see Table 3-14. The values obtained are in the range

of 192 W/(K*m²) to 343 W/(K*m²). This is a plausible range and therefore a strong indicator that process is limited, at least partially, by this heat transfer.¹²¹ If the main limitation lay in another process step the value would be much smaller.

Method	Quantity	unit	SSc-1	SSc-2	SSc-3	SSc-4
	t90	[s]	10.5	19	35	60
	X90	[g _{H2O}]	47	67	94	131
TDI	Р	[W]	14.3	11.3	8.6	7.0
LPJ	ΔT	[K]	22.0	21.4	19.8	19.2
	UA	[W/K]	0.7	0.5	0.4	0.4
	α	$[W/(K \cdot m^2)]$	343	278	228	192
	t 90	[s]	21	37	66	*
	X90	[gH2O]	41	54	77	*
LTJ-	Р	[W]	6.2	4.7	3.7	*
Ads	ΔT	[K]	11.0	10.3	9.9	*
	UA	[W/K]	0.6	0.5	0.4	*
	α	$[W/(K \cdot m^2)]$	299	239	198	*
	t 90	[s]	9	18	37	*
	X90	[g _{H2O}]	44	57	79	*
LTJ-	Р	[W]	15.6	10.1	6.8	*
Des	ΔT	[K]	16	15.1	14.6	*
	UA	[W/K]	1.0	0.7	0.5	*
	α	$[W/(K \cdot m^2)]$	515	353	246	*

 Table 3-14: Measurement results for large pressure jump adsorption and large temperature jump de- and adsorption measurements of small scale samples

* LTJ measurements were not carried out for small scale sample 4

Large temperature jump measurements

Samples SSc-1 to SSc-3 were characterized using large temperature jump measurements. The thinnest sample, SSc-1, needed 21 s for adsorption while the thickest coating on SSc-3 needed 66 s. Power is decreasing as a function of coating thickness. When looking at the increase of loading during adsorption, Figure 3.23 left, we see that the thinner sample SSc-1 adsorbed water faster than thicker samples. The different final pressures can again be contributed to the different absolute amounts of water adsorbed by the samples. The adsorption started a little earlier for thinner samples as well since the temperature jump from the cold plate needed a bit more time to cool down the thicker adsorbent layer. In Figure 3.23 right the pressure drop during adsorption is plotted. In the starting phase the thinner sample adsorbed a little more water than the thicker one, therefore its pressure dropped a little faster. Nevertheless the pressure drop of the thicker sample was nearly as fast and is sustained for a longer time. The sam-

ples power, which is proportional to the time derivative of the pressure are in the same range for all three samples. It was again approximated by linear fit of the dropping pressure for the time between 3 and 20 s. The slope of the fits ranged from 0.064 mbar/s for SSC-1 to 0.072 mbar/s for SSc-3. For an application in full scale adsorbers it can be deducted that in the starting phase the thicker coatings are able to deliver power in the range of thinner coatings. This is sustained over longer time but averaged over the whole time the delivered power is less for thicker coatings.



Figure 3.23: Pressure and relative loading as a function of time during LTJ adsorption.

In the desorption process we can observe a similar effect. When referring to the loading in Figure 3.24 left the thin coating layers changed their relative loadings faster. The overall amount of desorbed water, Figure 3.24 right, is again in the same range for the initial phase of the desorption.

If we assume that the process is limited by a resistance that is not a function of the adsorbent layer thickness but should be traceable to a feature of the coating that doesn't vary as a function of coating thickness the heat transfer between adsorbent layer and aluminum substrate or intraparticle diffusion in the adsorbent particles are two options. When considering an intraparticle diffusion coefficient of 10^{-11} m²/s measured for similar substances and a mean particle size of 1.8 µm with a narrow particle size distribution (d₉₀ =3.5 µm) as measured in chapter 3.3.2, the mass transport is fast and will not limit the process.¹²⁰ This points to the heat transfer between metal and adsorbent to be the limiting factor.



Figure 3.24: Pressure and relative loading as a function of time during LTJ desorption.

The difference in power output between the three applied measurement methods is partially caused by the difference in the available driving force. If one factors in this driving force difference and calculates the UA-values we can see that the relative spread between UA values is smaller than between the power values. A strong limitation of the process by mass transfer would lead to a higher spread in UA values. The heat and mass transfer steps relevant in this process are depicted in Figure 3.25. Thermal resistances that are not a function of the coating thickness are the thermal contact resistance between aluminum plate and the cold or hot plate, heat conduction in the aluminum plate, and the thermal contact resistance between coating and aluminum. The thermal conductivity of aluminum is in the range of $k = 238 \text{ W/(K \cdot m)}$ and the plate thickness is d = 2 mm. Measurements showed that the heat transfer coefficient between aluminum sample plate and the hot/cold plate is in the range of $\alpha = 2000 - 1000$ 5000 W/(K m²). For a given area of $A = 1480 \text{ mm}^2$ both resistances cannot govern the heat transfer limitation observed in these experiments otherwise the UA values would be significantly higher. Excluding these two, as well as all thickness dependent thermal resistances and intraparticle diffusion, we can draw the conclusion that the contact resistance between coating and aluminum sample plate is a major limitation to the adsorption process.

3



Figure 3.25: schematic representation of heat and mass transfer in the experiment with
1) Coating layer, 2) aluminum substrate, 3) hot/cold plate, a) mass transfer in the gas phase,
b) mass transfer in the coating layer, c) heat transfer in the coating layer, d) contact resistance
coating layer – aluminum substrate, e) heat transfer in the aluminum substrate and f) contact
resistance aluminum substrate – hot/cold plate.

This hypothesis has been supported by a simulation approach presented by Füldner et al. at the Impress Conference 2016. Each of the measurements was fitted to a matching simulation, see Figure 3.26, and the heat transfer of adsorbent layer to the aluminum plate was identified as a crucial parameter limiting the power output at the plateau. As can be seen in the bottom graph the simulations with a contact resistance lying in the range of $\alpha_{ads,mt} = 200 - 300 \text{ W/(K} \cdot \text{m}^2)$ give the best match to the experiment. Graphical representations are shown in Figure 3.26.



Figure 3.26: Simulation results and experimental results compared to each other for large pressure jump measurements (top) and parameter variation of the heat transfer between adsorbent layer and aluminum sample plate (bottom).

3.2.3.2 Large pressure jump measurements of full scale adsorbers

The full scale adsorbers were characterized in a large pressure jump testing rig. Here the adsorber is connected to a hydraulic cooling circuit, and suspended from a balance in an air tight measurement chamber. After desorption by reduced pressure to a predetermined loading point, a valve connecting the adsorber to an evaporator is opened and the test specimen starts to adsorb water. During adsorption the weight gain is recorded by the balance and the heat of adsorption is measured in the hydraulic cycle. For more information regarding the measurement procedure please refer to the experimental section in chapter 5.8.

Characterization of the adsorbers was carried out at two different temperature triples. To determine the adsorbers potential a first measurement series was carried out at mild conditions used for the preliminary tests with HX-A and HX-B. A temperature triple of $T_{L,I} = 10 \text{ }^{\circ}\text{C}$ evaporator temperature, $T_{M,I} = 35$ °C condenser and adsorption temperature and a desorption temperature equal to $T_{H, I} = 90$ °C was used. More challenging conditions were imposed on the adsorber in a second measurement series, here a temperature triple of $T_{L, II} = 4 \text{ }^{\circ}C$, $T_{M,II} = 39 \text{ °C}$ and $T_{H,II} = 110 \text{ °C}$ was used. The driving force for the second conditions were significantly lower as the water vapor pressure during the adsorption process was lower and the adsorber temperature higher. Results of the measurements were consistent over two measurements. The water uptake (m_{H2O}) , the time (t_{90}) and the adsorption power (P_{ads}) of the adsorbers for the t_{90} time interval are given in Table 3-15. The weight gain normalized to 1 for the measurements is shown in Figure 3.27 and Figure 3.28 left. It can be seen that with decreasing coating thickness the adsorbers are reaching their equilibrium states faster. The adsorption power output over time in Figure 3.27 and Figure 3.28 right shows that the peak power delivered is higher for thinner coatings but that the power of the thicker coatings is sustained over a longer time. The ideal power output would be a box function with a steady plateau and a sharp drop at the end.

Temperatures	Quantity	Unit	HX-1	HX-2	HX-3	HX-4	HX-5
	water uptake	[g]	11	36	55	80	99
	adsorption	[s]	104	288	288 484	684	2567
10/35/90 °C	time	[9]	101	200			2007
	adsorption	FW/1	367	415	385	384	121
	power	[••]	507		505		
	water uptake	[g]	11	36	55	80	99
	adsorption	[s]	210	1072	1737	3000	4725
4/39/110 °C	time	[3]	510	1072	1757	5007	4723
	adsorption	FW/1	115	102	94	74	38
	power	[**]	115	102	74	/+	50

Table 3-15: Measurement results for the full-scale adsorbers



Figure 3.27: Mass uptake and power output over time for the measurments at 90/35/10.



Figure 3.28: Mass uptake and power output over time for the measurments at 90/39/4.

The coatings absolute water uptake corresponded to a loading of $X = 0.18 \text{ g}_{\text{H2O}}/\text{g}_{\text{S}}$. When looking at the graph in Figure 3.29, top left, for the first measurements we can see that this water uptake is a perfectly linear function of the adsorbent mass on the heat exchanger. This confirms that even in the thickly coated adsorber all of the adsorbent is accessible to the adsorptive. In contrary to that, when plotting the adsorption time as a function of the adsorbent

mass, Figure 3.29, middle left, it can be seen, that there is a regime of linear relationship up to HX-4 but HX-5 does not lay in this regime anymore. This is reflected in the plot of mean power versus adsorbent mass. Here the power does not show a significant decrease in adsorption power up to HX-4 but for HX-5 we see a power drop by a factor of 3.2. These finding of a constant power output up to HX-4 are reproducing the effect observed in the preliminary studies that led to these experiments. Although the quantifications of the effect as COP is not possible from these measurements it is obvious qualitatively that by increasing the adsorbent mass and not varying the heat exchanger geometry and mass a higher energy efficiency can be achieved. In literature so far it was reported that this gain in energy efficiency would have to go hand in hand with a loss in power output because of a decrease in mass and heat transfer in the thicker coatings.^{20,76,77,117} It could be shown in this work, that with the coating and conditions used this is not the case. The adsorbent fill factor on the heat exchanger could be raised up to 382 kgs/m³ without sacrificing power output. At this power plateau, see Figure 3.29, bottom left, the powers measured between 367 W and 415 W correspond to a specific adsorption power of 257 to 290 W/L or specific cooling powers of 192 W/L to 221 W/L. In literature we can find specific cooling powers up to 225 W/L, for SAPO-34 coated heat exchangers,¹¹⁷ 101 W/L for aluminum fumarate coated heat exchangers ⁸⁶ and 289 W/L for CAU-10H coated heat exchangers.⁸⁴ It must be kept in mind that the power output is very sensible to the temperature conditions used. The measurements at more challenging conditions and therefore with less driving force available to the process show a different picture, see Figure 3.29, right. The adsorption time shows a steady increase, no power plateau is observable here. This is in accordance with literature. ^{20,76,77,117} Clearly here some other effects play a role. To reproduce this power plateau at other measurement conditions and raise the power at the plateau or extend the plateau to better ratios of heat exchanger to adsorbent mass ($r_{HX/S}$), it is crucial to gain some insight in the underlying processes.



Figure 3.29: Water uptake, adsorption time and power output as a function of the amount of adsorbent coated on the heat exchanger for measurements at 10/35/90 and 4/39/110 °C.

As for the small scale samples we can differentiate between heat and mass transport. At the power plateau mass transport cannot play a role since it would have to be a function of the coating layer thickness. Limitations from mass transport in the measurement chambers can be ruled out because its layout and sizes have been constructed accordingly. The single steps of heat conduction from the adsorbent to the hydraulic circuit are depicted in Figure 3.30. The heat transfer is subdivided in 6 main parts. Heat conduction in the coating layer, heat transfer from the coating layer to the lamella, heat conduction in the lamella, heat transfer from the lamella to the flat tube, heat conduction through the tube, and heat transfer from the tube to the fluid in the hydraulic circle. As for the small scale samples the heat conduction in the metal parts will not be limiting the process and heat transfer is in great parts limited by the heat conduction from the adsorbent layer to the fin.



Figure 3.30: Schematic representation of the adsorber with 1) coating layer, 2) aluminium lamella, 3) aluminium flat tube and 4) fluid channel. Heat transfer is depicted on the right side in blue starting with heat conduction in the coating, heat transfer from coating to the lamella, heat conduction in the lamella, heat transfer at the soldered contact from lamella to flat tube, heat conduction in the flat tube and heat transfer from flat tube to fluid.

In both, the small and the full scale measurements, it could be shown that the power output can be sustained at a high level while increasing adsorbent mass. This is because the process limitations here are the heat transfer between coating and lamella and not mass or heat transport in the coating layer itself. For very thick coatings or under more challenging conditions the limitations are different – here the power output is correlated to the coating thickness. A closer investigation of the boundary layer coating-lamella and adaption of the production process could increase the overall performance of the adsorber through a lowered contact resistance.

3.2.4 Density of different adsorbents

For the planning of an adsorber the mass of active material per adsorber volume is a key parameter and the coatings density is used for its calculation. Despite the simple concept of density, the determination of the actual value proofed difficult for coated layers of adsorbent. While the measurement of the samples dry weight was straight forward, for the determination of the sample volume sufficient precision was hard to achieve. Several methods have been evaluated and compared to each other for five different adsorbents using Silres® MP50E as a binder.

The most obvious approach is to have a coating sample, determine its area by geometrical considerations or with a microscope and its height by measurement of the coating layer thickness. This can then be used to calculate the coating volume and with its weight the density. The obtained values are given in Table 3-16 as "coated sample density" and are depicted in Figure 3.31 as "coating".

The volume of a liquid can be measured very precisely with a pycnometer. Trying to fill the coating into a pycnometer and determine the unfilled volume by filling up the residual volume with water did not yield any useful results. While in theory this approach is easy and very precise, practical challenges like bad wetting of the coating and coating particles clogging the capillary tube of the pycnometer rendered the method useless for density measurements.

Cuboidal blocks of coating were prepared. Here the volume can be determined by geometrical

considerations. There might be slight variations in the density of thin layers and blocks but nevertheless this method gives a good estimation of the density that can be achieved in a coating layer. The values are listed as "coating block density".

The volume for the bulk density was determined using a graduated cylinder. The concerning values are listed as "bulk densities".

The volume of adsorbent tablets, pressed at a pressure of 80 MPa into cylindrical tablets, has been determined to identify a maximum achievable density. The volume has been calculated from measurements of the tablets diameter and height, the concerning values are mentioned as "pressed tablet". All results are given in Table 3-16, and depicted in Figure 3.31.

Looking at the plot of the densities in Figure 3.31 we can see that the bulk densities were generally lower than the densities of coatings or pressed adsorbent. This was to expect here, the interparticle volume is bigger resulting in a lower density. The other method where the sample did not include the addition of a binder is the pressed tablets. It was expected that these show the upper limit of the achievable density. For SAPO-34 and CAU-10 the coating density was measured to be higher than this density. An explanation could be that the binder fills up the inter particle volume between the adsorbent crystals, so that the air gaps are filled with binder and the overall density increases. In general it can be seen that the densities for AlFum and CAU10-H belonging to the group of MOF's are considerably lower than those for the inorganic zeolite type adsorbents. This is important to keep in mind when comparing the water uptake of the adsorbents. The high water uptake per mass adsorbent that are often seen as one of the main positive aspects of MOFs are partially relativized by their lower densities when the goal is a high power compact device.

adsorbent	coated sample	coating block	bulk density	pressed tablet	
	density [g/cm ³]	density [g/cm ³]	[g/cm ³]	density [g/cm ³]	
TiAPSO	0.71	0.84	0.48	0.86	
SAPO-34	1 16	0.00	0.52	0.88	
(AQSA-Z02)	1.10	0.99	0.32	0.00	
AlFum	0.51	0.43	0.24	0.54	
Cau10-H	0.98	0.63	0.35	0.63*	
Na-Y	0.78	0.61	0.31	0.82	

 Table 3-16: Densities of adsorbents and their coatings determined with different methods



Figure 3.31: Coating and adsorbent densities measured with different methods.

3.3 Process optimization

3.3.1 Rheology

As elaborated in the theory section in chapter 1.3.2.4 the ability to control the slurry rheology is a key factor to improve coating performance and control the process. From the wide range of rheology additives available on the market a range of different additive types was chosen. The additives are listed in Table 3-17 together with their manufacturer and their chemical type. Out of this group of additives, those which were suitable for the use in adsorption heat transformation were to be selected. To achieve this, their thermal stability was tested and their influence on the coatings porosity and the rheology of the slurry was characterized. The results are presented in the next paragraphs.

rheology additive	suplier	type	
TEGO ViscoPlus 3060	Evonik		
Borchi Gel 0621	Borchers	organic, PU based	
Tafigel Pur 60	Münzing		
Rheovis AS 1956	BASF	organia aorrilia	
Tafigel AP 30	Münzing	organic, acrync	
BYK D420	BYK	organic, urea	
Optiflo H370 HV	BYK	organic, PEG based	
Optigel WX	BYK		
Optigel WH	BYK	inorganic, bentonite	
Bentone EW	Elementis		
HDK T30	Wacker	inorgania fumadailiaa	
HDK N20	Wacker	morganic, fumed sinca	

Table 3-17: Rheology additives to be tested, their supplier and chemical type

3.3.1.1 Thermal stability

As a first characterization of the additives the weight loss at elevated temperatures was determined with a moisture analyzer. Compared to the sophisticated thermogravimetric measurements used for the binders in chapter 3.1.1.2 the moisture analyzer proofed to be a simple and fast screening method to identify those substances, which will decompose at high temperatures. The measurements took considerably less time. The resulting weight losses are presented in Table 3-18 and Figure 3.32. The weight loss is given as the percentage of sample weight lost during heating. The values for dry mass or solid content of the additives were obtained from the supplier documentation. The weight loss relative to the dry mass accounts for the volatile solvents since many additives are delivered in dissolved form, see chapter 5.4.1 for details. Most of the organic additives showed a high weight loss druing heating. Rheovis AS 1956 and BYK D420 seem to be rather relatively stable at 200°C with a weight loss of 2.9 and 4.0 % of their dry mass. If one of the organic additives would have lost 100 % of its dry mass weight, it could be considered that this additive can be removed from the slurry by heating to 200°C. This implies that the additive can be used in the coating process and is removed during the curing step. Such an imaginary additive could be used safely in a coating but none of the additives characterized here lost 100 % of its dry mass. The negative value of -22.5 % weight loss relative to dry mass for Tafigel AP30 indicates that not all of the solvent was evaporated during the analysis. Most likely some of the solvent has been pyrolized during the heating process. The inorganic additives Bentone EW, Optigel WH, Optigel WX, HDK T30 and HDK N20 lost some weight which is surprising since, from a chemical point of view, they should be thermally stable and none of them is supplied dissolved or dispersed in a liq-

3

uid. A closer look shows, that the weight loss here is in the range of the moisture content of these additives.

Table 3-18: Rheology additives with their weight loss during heating to $200^{\circ}\mathrm{C}$ in the
screening procedure and where applicable the maximum water content according to the
supplier

rheology ad- ditive	supplier	weight loss [%wt]	dry mass [%]	weight loss rel- ative to dry mass [%]
TEGO Vis- coPlus 3060	Evonik	59.6	60	32.7
Borchi Gel 0621	Borchers	91.1	29.5	69.8
Tafigel Pur 60	Münzing	76.6	40	41.5
Rheovis AS 1956	BASF	17.5	85	2.9
Tafigel AP 30	Münzing	60.8	32	-22.5
BYK D420	BYK	56.8	45	4.0
Optigel WX	BYK	11.4	100*	11.4
Optigel WH	BYK	6.1	100**	6.1
Optiflo H370 HV	ВҮК	87.1	375	65.6
Bentone EW Elementis		5.1	100**	5.1
HDK T30	Wacker	2.3	100***	2.3
HDK N20	Wacker	2.1	100***	2.1

These substances can contain moisture up to * 13 %wt, ** 8 %wt, *** 1.5 %wt.



Figure 3.32:Weight loss relative to dry mass (turquoise) and weight loss (red) of rheological additives during heating in the moisture analyzer. For Tafigel AP 30 the weightloss relative to dry mass was below 0 %.

The more sophisticated thermogravimetric analysis has been performed on the inorganic additives which were to be most likely stable at higher temperatures in a reduced pressure environment. Results are shown in Figure 3.33. The fumed silica based additives, HDK T30 and HDK N20 showed no weight loss up to 500 °C. The initial offset is a result of the substances drying in the preconditioning step at 40 °C. As a result the signal starts below 100 %. In both measurements a drift in the weight signal can be observed, this is normal but usually not visible. Here the small sample mass because of the very low density of fumed silica together with the normalization makes this effect stand out for these two measurements. HDK T30 and HDK N20 can be assumed suitable for the use in coating slurries for adsorption heat transformation technology.

The bentonite based slurries Optigel WH and Bentone EW showed a slight weight loss in the order of 5 % at relatively low temperatures. Most of this weight loss happens during the preconditioning step at 40 °C in a dry gas stream resulting in starting values below 100 %. The rest of the weight loss takes place at rather low temperatures as well. Since the water adsorption of these bentonites lies in the same range, it is very probable, that the lost mass is only water. This would not be a problem in an adsorption process with water as the adsorptive. Here the additives could be used safely.

Optigel WX shows a profound weight loss over the course of the measurement. The weight loss can be subdivided into two distinct steps. In the first step about 10 % of the sample weight is lost. This corresponds to the weight loss observed in the screening test. At higher temperatures another weight loss step could be observed. The supplied documentation states

that there are no adjuvants used in this products. Nevertheless since this weight loss cannot be clearly contributed to a loss of water which should be at lower temperatures, Optigel WX was ruled out for the application in the vacuum environment of adsorption heat transformation technology.



Figure 3.33: Thermogravimetric analysis of the inorganic rheology additives.

To proof the assumption that the bentonite type additives themselves do not decompose, XRD measurements have been performed on the concerning additives at room temperature and in situ at 200°C. Powder diffraction patterns are depicted in Figure 3.34. No structural change could be observed in either of the concerning sample. This is a strong indicator that no decomposition of the substances takes place, neither for Bentone EW nor for Optigel WH or Optigel WX.

It can be concluded that from a thermal point of view four additives are suitable for the use in adsorption heat transformation technology: Optigel WH, Bentone EW, HDK T30 and HDK N20. Optigel WX but was ruled out because of an unidentifiable weight loss in the thermo-gravimetric analysis.



Figure 3.34: X-ray powder diffraction patterns for Optigel WX, Optgel WH and Bentone EW at 25 and 200 °C. Diffraction at 200 °C was shifted upwards for better comparability.

3.3.1.2 Influence on porosity

The influence of the additives on the coatings porosity was characterized using nitrogen sorption measurements. The pore volume and BET surface of the resulting coating in Table 3-19 and Figure 3.35 show that the additives had a slight influence on the coatings porosity. It is clear, though, that none of the additives obstructs the pores in such a way that the resulting coating could not be used. Optigel WH and Bentone EW seem to add some porosity to the coating. One explanation for this effect is that a part of the binder is adsorbed on the surface of the bentonite particles. Normally this binder would have blocked some part of the adsorbent pores as can be seen by comparing the surface area of the pure adsorbent (dashed line) and the surface area of the coating with no additive in Figure 3.35. The binder that is adsorbed on the bentonite particles does not block the adsorbent so that the overall surface area and the total pore volume are increased compared to a coating with no rheology additive. Another explanation is that the flake like particles of the additive form additional pores, likely interparticle volume. From a porosity point of view all additives are suitable for an adsorptive coating. It should be pointed out that the concentrations of the additives in the coatings are different because the concentrations to achieve a desired rheological effect are different as well. Therefore comparing the additives at concentrations which are likely to be used in a final slurry is the most appropriate way and was done in this work.

additive	concentration [%wt]	BET surface area [m²/g]	total pore vol- ume [cm ³ /g]	p/p ₀
Tego Visco Plus 3060	1	570	0.23	0.95
Borchi Gel 0621	3	532	0.22	0.95
Tafigel Pur 60	2	526	0.21	0.95
Rheovis AS1956	3.5	473	0.19	0.95
Tafigel AP30	0.5	611	0.24	0.95
Optiflow H3070HV	0.75	602	0.24	0.95
Optigel WX	3	552	0.22	0.95
Optigel WH	1.75	669	0.27	0.95
Bentone EW	1	628	0.25	0.95
HDK T30	2	593	0.25	0.95
HDK N20	2	578	0.23	0.95
no additive	0	608	0.24	0.95

 Table 3-19: BET surface area and total pore volume of coatings with different rheology additives



Figure 3.35: BET surface area (left) and pore volume (right) of the coatings using different additives – the value for the pure adsorbent is shown as a dashed line.

For the coating of full scale adsorbers Optigel WH was chosen because of its good performance and availability in small lab and production size quantities. An additional measurement of the water sorption isotherms of a TiAPSO coating with Optigel WH as rheology additive was carried out to confirm the nitrogen sorption measurements and to ensure that the water uptake is not severely diminished except from the introduction of inert mass. The measurement is depicted in Figure 3.36 and compared to the pure adsorbent. The slight shift of the additive coatings isotherm to higher relative pressures can be contributed to the binder and has been observed before. The peak at the end of the no additive curve is due to capillary condensation, and does not play a role in the actual process. The full scale adsorbers coated with a rheology additive containing slurry could be successfully characterized in the LPJ test rig at Fraunhofer ISE, as shown in chapter 3.2.





Figure 3.36: Water isotherems of pure adsorbent and of a coating with rheology additive, corrected for binder and additive content.

3.3.1.3 Slurry rheology

Analytical challenges in slurry rheology measurements

When characterizing the slurry rheology itself and the influence of the additives on the slurry rheology, some challenges arose compared to a straight forward measurement of typical fluids. The challenges and how they were addressed in the measurements were as follows.

Disposable measurement geometries had to be used because of the binders ability to adhere to measurement equipment and because of the fine and hard zeolite particles that have a grinding effect on the aluminum surface of the measurement device. After several measurements slight scratches in the surface of the measurement tool could be observed, Figure 3.37 (left). Disposable measurement devices are not offered in every form – a cup measurement device, which would have been the tool of choice to minimize the drying of the slurry was not available as a disposable geometry. Instead a disposable plate-plate geometry has been chosen.



Figure 3.37: scratched measurement plate (left), transient effects (middle) and artefacts because of drying coating (right).

The presence of adsorbent increased the evaporation rate of the water based slurries. The resulting fast drying of the slurry limited the time available for a measurement before drying effects distorted the results. The drying took place at the outer rim of the measurement plates where the slurry thickened or even dried out completely. This lead to artefacts in the measurement as shown in Figure 3.37, right. With shorter measurement times this effect became negligible. One approach to speed up the measurement was to shorten the sampling time for each measurement point. This was not possible in the low shear region because for low shear rates some time is needed to develop a homogeneous flow field in the measurement geometry. Otherwise transient effects arise that make the viscosity appear lower than it is, Figure 3.37 middle. As a result a compromise between sufficient sampling time and short overall measurement time had to be found. Alternatively the measurement time can be cut down by decreasing the resolution concerning the shear rate as well. The sampling time for individual points can then be increased proportionally without increasing the overall measurement time. Nevertheless all of these approaches have specific drawbacks. Another solution to prevent drying out of the slurry is to decrease the measurement temperature. The decreased temperature has a minimal effect on the slurry viscosity, as will be shown later. It can be assumed that, on one hand, the effect is similar for all samples and therefore does not change the relative results when comparing slurries. On the other hand, the effect is so small compared to other effects so that it is insignificant and neglectable. Decreasing the temperature to 15 °C to slow down the evaporation of water from the slurry proofed to be the best way to perform good, repeatable measurements without sacrificing accuracy or resolution. At temperatures below room temperature it must be ensured that no condensation into the slurry takes place. This will have a thinning effect decreasing the slurries viscosity.

The time between preparation of the slurry sample and measurement must be kept short. Even with proper agitation of the slurry an agglomeration effect can occur that influences the rheology of the sample.

Shear rate dependend viscosity

The whole range of organic additives has been characterized rheologically. The additive was added to a slurry of CBV-300 and Silres® MP50E and the viscosity of the slurry was meas-

theses additives behave similarly. Rheovis AS 1956 has a less shear thinning character than the other ones. There were no further investigations carried out on these additives since they showed no promising results in the thermal stability test.



Figure 3.38: Slurry rheology of slurries with different additives.

The inorganic additives that were found to be suited for the use in adsorption heat transformation technology were characterized more thoroughly using TiAPSO as adsorbent which had emerged as the adsorbent of choice for many adsorption heat transformation applications. Here the slurry rheology at different concentrations of the additive was measured. This allows to intra- or extrapolate the effect of different amounts of additive. This is helpful when trying to formulate a slurry with certain predetermined rheological properties. The bentonite based additives have all been characterized with the same concentration. The fumed silica based additives did not show an effect of the desired magnitude in this range of concentrations so that those have been characterized with higher additive concentrations.

Similar to organic additives the bentonite based additives induced a shear thinning behavior to the slurry see Figure 3.39. Bentone EW shows a moderate increase in viscosity with an increasing concentration of the additive. The sensitivity of the effect is slightly higher at lower shear rates.

Optigel WX raised the viscosity considerably more compared to Bentone EW. This was especially true for the higher concentrated slurries. The effect per mass additive is higher here. It could be assumed that this allows to use less rheology additive and thus more adsorbent in the slurry, but the effect is small since the saving of 0.125 %wt additive in regards to slurry weight will result in about 0.5 %wt more adsorbent in the actual coating. Optigel WX additionally developed a plateau at a shear rate of about 1 to 5 s⁻¹ for a concentration of 0.25 %wt. This plateau shifted to higher shear rates with increasing concentrations of additive. A plateau at a shear rate of 6 to 25 s⁻¹ was observed for a concentration of 0.5 %wt.

Optigel WH induced a shear thinning effect too, it is nearly independent of the concentration in the concentration range investigated here. The effect to mass ratio was slightly less than for Bentone EW.

An imaginary ideal flow curve for the dipcoating of an adsorber with small structures is depicted in Figure 3.39 on the bottom left for bigger structures an slightly higher viscosity is tolerable.



conentration [%wt] — 0.250 — 0.375 — 0.500

Figure 3.39: Concentration dependend shear thinning effects for temperature stable inorganic additives.

HDK T30 showed a rise in viscosity and a shear thinning effect, dependent on the additives concentration, compare Figure 3.40, left. Similarly to Optigel WX a viscosity plateau could be observed that shifted to higher shear rates with increasing additive concentration. The

slight distortion at the plateau for the highest concentrated slurry is most likely the effect of bubbles that formed in the highly viscous liquid during homogenization and cannot be removed completely from the sample.

HDK N20 shows a very pronounced viscosity plateau for higher concentrations, see Figure 3.40, right. Shear thickening effects were observed in the shear rate range of 10 to 100 s⁻¹. This surprising effect is reproducible and hence not a measurement error. It can be assumed that the chain like molecular structure of the fumed silica that does not only build up intermolecular networks by hydrogen bonds but also can lead to entanglement of the chains. Similar effect were measured by Skelhon in fruit juice formulations for chocolate confectionary using the same additive.¹²²





From the selection of rheological additives several could be identified as suitable for the use in adsorption heat transformation coatings – Bentone EW, Otigel WH, HDK T30 and HDK T20. Their rheological properties have been thoroughly characterized and their thermal stability and influence on the porosity was checked.

Temperature dependent viscosity

During the preparation of the coating the dry adsorbent is mixed with water and consequently the heat of adsorption is set free in the process. This heats up the slurry, temperatures of 40 °C were measured. The temperature dropped during the coating process because of heat losses to the environment. The viscosity of a liquid is typically a function of temperature and the viscosity is lower at higher temperatures. Therefore it was investigated whether and to what ex-

tend this effect would appear in the coating slurry. The slurry viscosity was measured at different temperatures. The results are depicted in Figure 3.41 (top left). The measurements showed a different effect than anticipated. The viscosity increased for a temperature rise from 20 °C to 30 °C. For the measurement at 40 °C a further rise of the viscosity was observed and several artefacts in the rheology curve appeared. The reason for these artefacts is evaporation of water from the slurry due to the elevated temperature. At the edge of the measurement plate the coating dried out and small particles formed which were the causes of the artefacts observed. The same drying effect probably led to the small rise in viscosity at 30 °C instead of the anticipated small drop in viscosity. Even if there was a considerable drop in viscosity as a result of the rising temperature, the effect is small compared to the effect of the drying edge. This indicates that the temperature dependency of the slurry viscosity doesn't play a significant role in the real coating process.



Figure 3.41: Shearrate dependend viscosity for different temperatures, temperature dependend viscosity at different shearrates and shearrate dependend viscosity for different water contents.

Another approach was used to confirm this assumption. A temperature ramp at a fixed shear rate was measured. Here the time at elevated temperatures is shorter and the sample is not subjected to elevated temperatures during the preparation of the measurement, thus limiting the amount of evaporation. The result is displayed in Figure 3.41 (top right). For the measurement at a shear rate of 0.1/s the viscosity started at a plateau, then the viscosity began to rise and artefacts appeared. For this measurement as well, the edge started to dry. Sampling time was reduced by measuring at a higher shear rate. For the measurement at a shear rate of 1/s the measurement at a shear rate of 1/s the next measurement at a shear rate of 10/s the viscosity is slightly rising as a function of temperature. The effect seems to be consistent over the course of the temperature ramp.

It can be concluded that, in the temperature range that the slurry will have in the coating process - 25 to 35 °C, the slurries viscosity is not altered significantly. Drying processes however will play a role. The influence of differences in water content has therefore been characterized using a slurry containing no rheology additives. The results are shown in Figure 3.41 (bottom left). As expected a lower water content lead to a rise in viscosity of the slurry. This was proven with actual samples from the coating of a full scale adsorber. A spray coating slurries rheology was measured before and after the coating process, see chapter 3.3.3.2. Summarizing the findings it can be stated that during the preparation and handling of the slurry, excessive evaporation of the water should be avoided to keep the rheological profile of the slurry intact.

Yield stress of the coating slurry

The yield stress is the minimal shear stress that is needed to make the slurry start to flow. It influences the slurry stability concerning reagglomeration and sedimentation of the particles, see chapter 3.3.1.3. For a spray coating slurry the yield stress was determined to check whether it could be expected that the slurry would stay dispersed when stored for longer timers.

Two commonly used methods to determine the yield stress were applied. For the first method the shear stress was measured as a function of the shear rate. Fitting to the Herschel-Bulkley model used for non-newtonian fluids gave the yield stress. The model expresses the shear stress using the yield stress, a consistency factor K and a shear thinning index (n), it is presented in the introduction in chapter 1.3.2.4. Other methods like the Bingham and Casson model gave worse fitting correlations. The yield stress obtained by fitting to the Herschel Bulkley Model was $\tau_0 = 4$ Pa. The measurement and the fit are depicted in Figure 3.42 (right). It can be seen that the fit slightly overestimates the real yield point. The slurry is somewhat stable against sedimentation but for long term stability a higher yield point of above 10 Pa is needed. This correlates to long term observations on the slurry investigated here. The slurry was stable for several hours during the coating process but after two weeks a separation into a

more liquid and a denser phase could be observed. This separation was reversible and the slurry could be redispersed by thorough stirring.



Figure 3.42: stress ramp for yield stress determination – no distinct slope change can be observed (left). Shear stress as a function of shear rate for the determination of the yield stress (right).

Applying the second method the slurries deformation or shear strain was characterized as a function of the stress applied to the slurry, see Figure 3.42. For a fluid exhibiting yield stress a curve with two distinctly different slopes would be expected – a very slow rising plateau of shear strain in the region where the applied stress does not exceed the yield stress and a steep rise after the yield stress has been reached. This behavior cannot be observed in the measurement below. This characterization method was therefore dismissed as unsuitable for the characterization of the yield stress in this slurry.

We can conclude that the low shear viscosity of a spray coating slurry is not sufficient to prevent long term sedimentation of the adsorbent. For improved slurry stability the low shear viscosity could be raised – this would on the other hand impact the coating performance. Another option for stabilization against sedimentation is the addition of a dispersion additive. This has been successfully demonstrated in project works for adsorptive coatings that are used in open dehumidification were the thermal stability of the additive is not of such a concern.

Thixotropic behavior of the coating slurry

The time dependency of the recovering viscosity after high shear rates dictates levelling and sagging behavior, see chapter 1.3.2.4. A viscous slurry as used for spray coating applications

was characterized by subjecting the sample to a shear stress step function and measuring the response function of the viscosity, see Figure 3.43.



Figure 3.43: Viscosity as a response to a shear stress step function and the following recuperation of viscosity.

The low shear viscosity in the undisturbed segment (red) was at a plateau of 1750 Pa s. During the high shear distortion segment a sharp drop in viscosity could be observed owing to the destruction of the internal structure (green). The viscosity was restored nearly instantly. The sampling time for the first recovery point was 5 s. During that time the plateau value had been reached already (blue). The sampling time cannot be decreased without distortion of the measured viscosity. A certain part of the inner structure seems to be permanently distorted, a recuperation to the initial value was not observed. For a longer measurement time the viscosity rose again, but this effect can be contributed to drying out of the slurry in the measurement geometry.

Similar observations could be made in the ORO measurement where the undisturbed and recovery phases are characterized by an oscillatory measurement. The results are depicted in Figure 3.44. The measurement in the initial phase has some influence on the slurries structure already, the young modulus decreases. After the rotational distortion the young modulus needs about 20 s to reach a plateau value which is considerably lower than the initial value. Summing up we can state that there is no pronounced thixotrophy to be observed in the investigated slurry. Characterization of slurries with smaller concentrations of the rheology additives yielded the same result.



Figure 3.44: Young modulus for an ORO measurement to characterize the slurry thixotrophy.

3.3.2 Particle size and deagglomeration

Supersonic deagglomeration of the adsorbent particles is part of the slurry preparation process. This process step was introduced due to empirical observations and works well, but the results were never comprehensively investigated and quantified. It could be observed for some adsorbents, that a deagglomeration step was essential to prevent clogging of the spray coating nozzle. Furthermore, as a rule of thumb the adsorbent particles should be in the order of 10 µm or below to assure that intraparticle diffusion can be completed during the adsorption process and does not limit the adsorption process. The deagglomeration process was characterized by particle size distribution measurements to gain insight into the resulting changes and to understand whether deagglomeration is necessary, especially with regards to scaling up of the deagglomeration process. Dispersions of the most common adsorbents – TiAPSO, SAPO-34, Na-Y Zeolithe, NH3-Y Zeolithe and aluminum fumarate have been characeterized. All of these adsorbents are commercially available and synthesized in large scale industrial processes. The deaglomeration was varied between "without deaglomeration", "with supersonic deaglomeration at 45 kHz", as used in the full scale coating process and "with megasonic deaglomeration at 1 MHz" for an even more intense deagglomeration.

The resulting particle size distributions are depicted in Figure 3.45. For the TiAPSO adsorbent the particle size distribution can be approximated as monomodal, Figure 3.45 top left. The mean particle diameter was about 2 μ m. All of the samples show the same distribution regardless of the deagglomeration process. Therefore it can be assumed that no agglomeration occurred or that the agglomerated particles were deagglomerated by conventional stirring. When scaling up the coating process to industrial scales this adsorbent can be used without a

dedicated deagglomeration process step, saving processing time and equipment costs.

The Na-Y type zeolite showed a similar nearly monomodal particle size distribution as the TiAPSO, Figure 3.45 top middle. Its mean particle diameter at 3 μ m was slightly higher and the overall distribution is broader. It included particles up to ~15 μ m. The particle size distribution is independent from the deagglomeration process. The process can be scaled up without using special deagglomeration equipment.

The SAPO-34 adsorbent showed a bimodal particle size distribution for the non deagglomerated samples, Figure 3.45 top right. While the main fraction had a mean particle diameter of 3 μ m a smaller fraction with significantly larger particle diameters of 50 μ m to 300 μ m existed. This corresponds to the observations made in spray coating trials. Using this adsorbent, the nozzle would block without a deagglomeration step. Both supersonic and megasonic deagglomeration are able to deagglomerate these particles.



Figure 3.45: Particle size distribution of different adsorbent with and without deagglomeration, log-scale x achsis.

The ammonium exchanged Y Type zeolite, NH3-Y, showed a much broader particle size distribution than the TiAPSO and SAPO-34 samples. The deagglomeration process altered the distribution function. The biggest fraction of particles can be deagglomerated using either ultrasonic or megasonic deagglomeration processes.

The aluminum fumarate showed the most inhomogeneous particle size distribution of all samples characterized. The volume fraction of particles larger than 10 μ m made up the largest part of the particles. While supersonic and megasonic deagglomeration achieve to deagglomerate some of the agglomerates, it is clearly visible that this processes are not suited if a mean particle size in the order of around 5 μ m is desired. The coating process can be adapted to these larger particle sizes but if for other reasons smaller particle sizes are needed the aluminum fumarate production process should be adapted.

3.3.3 Coating techniques

3.3.3.1 Dip coating of high surface area heat exchanger

At the beginning of this thesis, dip coating was the coating procedure of choice. It was expected that future heat exchanger designs would incorporate foam like metal structures that have a very high surface area compared to conventional heat exchangers while still maintaining good heat conductivity. For these complex geometries dip coating is the only possible technique because with other coating techniques the slurry cannot penetrate the structure. A good wetting of the substrate and a low viscosity of the coating slurry is the key to successful dip coating of these structures. Several full scale heat exchangers of high surface area metal structures have been coated with TiAPSO as adsorbent and Silres® MP50E as binder, an example is presented here.

The heat exchanger consisted of aluminum fibers sintered together and cut into pieces. These pieces were then soldered in between flat tubes, see Figure 3.46 left. The heat exchanger was constructed by Fraunhofer IFAM in Dresden in cooperation with Haugg Industriekühler GmbH. Preliminary tests showed that the coating slurry was able to penetrate the porous fiber structures, see Figure 3.46 middle. The full scale dip coating was carried out in three consecutive coating and drying steps. Results are listed in Table 3-20. The objective was to keep the mass ratio low by trying to deposit high amounts of coating on the heat exchanger. Visual inspections showed that at some places the open foam structure of the adsorber is blocked by the coating, see Figure 3.46 right. Nevertheless large pressure jump measurements of the adsorber to the adsorber is still well accessible.



Figure 3.46: Drawing of the high surface area adsorber with flat tubes at the sides sandwiching the fiber metal pieces (left), cross cut through a coated piece of coated metal fibers showing the accessibility of the structure for the slurry penetration in dip coating (middle) and image of a position at which the coating complicates gas access to the inner part of the adsorber (right).

quantity	unit	metal fiber adsorber
dimensions	mm ³	$97 \times 97 \times 340$
volume coatable structure	L	2.49
volume complete HX	L	3.20
mass HX	kg	2.84
mass adsorbent	g	263
mass ratio	$kg_{\rm HX}/kg_{\rm S}$	10.8
fill factor	kgs/m ³	82

Table 3-20: Results for the coated heat exchanger

Large pressure jump measurements have been performed to characterize the adsorbers performance. The mass uptake for adsorption at temperatures of 90/35/10 °C is shown in Figure 3.47. The resulting mean power, calculated as explained in the experimental section in chapter 5.8.2, of 483 W is comparable to state of the art plate fin heat exchangers but not significantly better.


Figure 3.47: Mass uptake and power output of the metal fiber adsorber during large pressure jump measurements at temperatures of 90/35/10 °C, up to a time of 750 s.

The high mass ratio and low fill factor of this adsorber indicate that these foam like metal structures are not the structures of choice when using a binder based coating approach. The power output does not significantly exceed that of an adsorber made from a state of the art heat exchanger as presented in chapter 3.2.

Heat exchangers using fiber metal structures are still subject to research and in the process of optimization. While plans for a scale up and production are emerging, so far there is no option to obtain these structures in constant quality and bigger numbers. Because of the complex production their price remains too high for a near term application in industrial scale. These high surface area structures show an improvement in performance compared to conventional heat exchanger designs in a direct coating approach. This did not apply to binder based coatings. As shown in chapter 3.2.4 the binder based coating densities lie in the range of 0.7 g/ml while coatings from direct crystallization processes approach the density of the pure adsorbent. This translates to a lower fill factor for binder based coatings on fiber metal structures when the accessibility of the adsorbent is maintained. It can be concluded, that the performance of the binder based coating on the metal foam adsorber is good but it can be achieved with state of the art heat exchanger structures as well. Considering that the price of state of the art heat exchangers is roughly one order of magnitude lower and that they are readily available on industrial scale, the metal fiber adsorber is not an option at this point of time .

The coating of conventional heat exchanger structures using the dip coating process was possible but several challenges arose.

The coating had to be carried out in several consecutive dip coating steps, layering them up

100

until the desired amount of adsorbent was reached. The amount of coating deposited varied with each step as the geometry of the adsorber was changed by the coating process. Small gaps and spaces between fins and lamellas became smaller with each coating step and were then prone to complete blocking with adsorbent, decreasing the accessibility from the gas phase in the final adsorber, see Figure 3.48. This made controlling the final adsorbent weight hard and the possibility of blocked pores rose.



Figure 3.48: Blocked fins in a dip coated adsorber.

Another drawback of the dip coating process was the enormous amount of slurry needed to coat the heat exchangers. The whole heat exchanger had to be submerged in the slurry – therefore the amount of slurry that was used had to be sufficient to fill out the volume of a container big enough to fit the heat exchanger. Additionally the amount to be deposited on the adsorber had to be considered. Twice as much slurry as deposited on the heat exchanger was needed to be prepared in a typical coating experiment. The left over coating slurry had to be disposed. While this effect becomes insignificant when coating several hundreds of heat exchangers in a production process, for research purposes it is a big drawback. Especially for adsorbents that are not available in large quantities or still expensive, a way to coat a single heat exchanger with lower amounts of adsorbent wasted would facilitate and speed up research activities.

Despite these drawbacks the dip coating process can yield good results when applied correctly as shown in chapter 3.2.2.2. For the binder based coating of flat tube lamella heat exchangers or porous metal structures it is the method of choice because of its ability to intrude small pores and structures.

3.3.3.2 Spray coating

The spray coating process had been initially dismissed, because it is not suited to coat complex foam like structures. When it became clear that the adsorbers to be coated in a real application would be standard heat exchangers with less complex structures, spray coating was reconsidered. Indeed, it allows eliminating some of the drawbacks of dip coating. The amount of slurry that is prepared can be custom tailored to the amount applied to the heat exchangers. Less slurry has to be discarded after the coating process saving valuable material and opening up the possibility to coat with adsorbent only available in small amounts. This could be demonstrated with a MIL-160(Al) adsorbent. In the spray coating process the amount of slurry deposited on the heat exchanger can be fine-tuned and continuously visually monitored during application of the slurry. There is no danger of blocking all of the access gas voids in a last coating step as for the dip coating process.

Scale up of spray coating

First steps and preliminary test have been made using a low-tech air brush spray gun. The resulting coatings were suitable as a proof of concept but blocking of spray gun and incompatibility with several adsorbents due to their particle sizes made coating of full adsorbers impossible and showed the need for further improvements. The spray gun was changed to a professional high volume low pressure (HVLP) spray gun with different nozzle sizes to avoid blocking. A built in filter was added to keep agglomerates from entering the spray gun. To remove the particles from the slurry a sieving step had to be introduced. Sieving of the powdered adsorbent before slurry preparation improved the clogging problem but still aggregates would form and occasional clogging occurred. Filtration of the ready-made slurry in a 125 µm filter before application turned out to be the most suitable option. Using Optigel WH, a rheology additive that was approved for the use in adsorption heat transformation technology in chapter 3.3.1, the coatings viscosity in the low shear regime was raised. This allows for a good buildup of the coating layer and prevents reagglomeration of the adsorbent particles. After successful spray coating of small scale samples, full scale adsorbers were spray coated, see Figure 3.49 (left). For these geometries it was important to keep a small working distance between spray gun and adsorber and work with enough pressure to prevent the slurry from being deposited only on the edge of the fins. The full scale adsorbers were characterized in an open sorption process by Denco Happel as exemplified in Figure 3.49 right. The measurement results are discussed below.



Figure 3.49: Close up of a spray coated adsorber (left) and principle of open air dehumidification (right).

The prepared heat exchangers were characterized in test rig at the research facilities of Denco Happel, an industrial partner. Exemplary results are discussed. For the measurement moist air with an initial temperature of 32 °C and an initial humidity of 25 g_{H2O}/kg_{air} was passed through 2 adsorbers in series. The adsorber temperature was controlled by a hydraulic circuit and set to 70 °C for desorption and 40 °C for adsorption. In Figure 3.50 the measured absolute

humidity and the air temperature at the air inlet and outlet as well as the water feed and return temperature are plotted as a function of time. For the adsorption phase a sharp drop in the outlets air humidity down to 9 g_{H2O}/kg_{air} was measured. With increasing time the adsorbent became more and more saturated, the adsorptions rate decreased until no net adsorption took place anymore. The air outlet temperature dropped to 38 °C during the adsorption phase. This seems counterintuitive since heat is generated in the adsorption process. The explanation is that the heat was dissipated through the heat exchanger into the hydraulic circuit and the cooling overcompensated for the heat production in the adsorbent. In the beginning of the adsorption phase the adsorption heat and the sensible heat stored in the adsorber parts were dissipated into the hydraulic circuit. At the end of the adsorption process where all sensible heat had already been dissipated and less heat of adsorption was generated, the adsorber acted more and more as an air-water heat exchanger heating the inlet air from 32 °C to 38 °C. The adsorbers performed as expected, spray coating can therefore be seen as a feasible coating method. It has been demonstrated for various adsorbents including TiAPOS, Na-Y Zeolithe, SAPO-34, NH3-Y Zeolite, CAU-10H and MIL-160(AI).





Changes in the coating slurry during processing

As already discussed in chapter 3.3.1, the slurries properties changed during processing. There are three main issues to consider, reagglomeration, drying and air entrapment. Reagglomeration occurs when particles in the slurry clog together and form agglomerates. This is a natural tendency in the slurry driven by gravitational forces and the particles tendency to minimize their surface energy in water. It can be counteracted by intense stirring, raising the low shear viscosity, and appropriate surfactants also known as dispersion additives. Dispersion additives could be used successfully in several trial coatings and have been shown not to alter the performance of open dehumidification systems. No quantitative investigation was carried out on their ability to stabilize the slurry since they are not applicable to adsorption heat transformation applications due to insufficient thermal stability.

The second issue, drying, occurs due to evaporation of water during the processing time. The

water content of the slurry has been measured for a slurry that has just been prepared and for the same slurry after the spray coating process that lasted for about 4 hours. A drop in water content of 2.6 %wt over the processing time was observed. It can be prevented by customized stirring equipment that suppresses air exchange with the surrounding while allowing to stir the slurry. This significantly decreases the evaporation rate in the slurry. Another method is to replace the evaporated water in the slurry. Air entrapment, or so called micro foam, is favored by higher slurry viscosities and the constant stirring of the slurry which is done to minimize reagglomeration. The stirring introduces air bubbles in the slurry. Due to the considerable viscosity of viscous slurries the drag force on the bubbles increases. This is caused by the same effect as explained for sedimentation in chapter 1.3.2.4. Additionally the stirring leads to fine small bubbles that are even harder to remove from the slurry. The radius of the bubbles is included with a power of two in the calculation of rising speed stokes law and therefore has a significant effect on the stabilization of these bubbles. To quantify this air entrapment the slurry density has been measured before and after the spray coating process. The densities were $\rho_{\text{start}} = 1.4 \text{ g/ml}$ and $\rho_{\text{end}} = 1.0 \text{ g/ml}$. The slurry density decreased to only 70 % of its initial value. This effect is counteracted by the drying effect discussed above. The effected can be minimized by so called deaerators that prevent surfactants from stabilizing the air-slurry interface and promote the diffusion of air from smaller into larger bubbles. Diffusion is taking place because of the difference in the La Place pressure in bubbles resulting in a shrinkage of small and growth of bigger bubbles which are easier to remove.

Additionally to these findings the slurry viscosity was measured for a slurry sample from the start and end of the spray coating process. The resulting flow curve is shown in Figure 3.51. The viscosity rose significantly, here the effects of air entrapment and reduced water content both play a role. Although these effects are shown here for a spray coating slurry here they apply in a similar way to dip coating slurries. Slurries with lower viscosities are more prone to reagglomeration of the adsorbent particles but less prone to air entrapment.



Figure 3.51: Shear rate dependent viscosity of the coating slurry at the start and end of the spray coating process.

3.3.3.3 Screen printing

Both the dip- and spray-coating process are well suited for coating large parts such as the heat exchangers. However they lack the ability to exactly replicate high resolution coating patterns. Applications that need precise deposition of small amounts of coating slurry call for a different coating method. One of such applications is the manufacturing of adsorbent based sensors currently under investigation. The screen printing process can be readily applied here. By developing a suited screen printing paste containing the adsorbent, the screen printing process can be used as a plugin solution into existing processes.

A water based adsorbent containing paste has been developed for the use in screen printing. First test prints have been carried out at the Fraunhofer IFAM in Dresden. The tests were successful but the printed layer showed defects like pinholes and foam bubbles, see Figure 3.52 left. These defects can have a wide variety of causes - improper wetting, improper drying, improper dispersion or unsuited rheological properties. This paste was developed according to guiding values for screen printing paste. In a completely new attempt with a different binder and additive system a different approach was taken. A commercially available screen printing paste was characterized and the new formulation was made to closely match its characteristic rheology profile, see Figure 3.53. A three roller mill was used for better homogenization and dispersion of the adsorbent in the paste. The foam bubble formation observed earlier could be successfully suppressed with the new formulation. Nevertheless, the printing resolution did not match the one achieved with the highly sophisticated equipment at IFAM Dresden.



Figure 3.52: Test print at IFAM Dresden, pinholes and foam bubbles are discernable (left and middle). Test print at Fraunhofer ISE (right).



Figure 3.53: Rheological Profile, of commercial screen printing paste and the screen printing paste using Na-Y zeolite – with and without homogenization in a three roller mill.

4 Summary

In this thesis adsorptive coatings were developed with a focus on binder evaluation, improvement of efficiency at high power oputputs and optimization of the coating process. A total of thirteen different silicone binders with different curing mechanisms, different dispersion media and different molecular structures were characterized. Four of these binders showed a very good thermal stability with weight loss onset points of over 400 °C. The best binders affected the porosity of the adsorbent only slightly. A remaining porosity of up to 74 % was achieved, with 85 % being the best possible value. The best binders reported in literature achieve a remaining porosity of 58 %. The mechanical performance of the binders was characterized by adapting tests from the varnish industry to adsorptive coatings. Altogether, Silres® MP50E was identified as the most suitable silicone binder for further experiments. It has outstanding pore accessibility, a good thermal stability. It is water based and therefore much safer to handle than other solvent based binders. The group of room temperature curing binders was found to be unsuitable for heat transformation applications.

Inorganic binders were tested because of their superior thermal stability that allows for high efficiency heat pumps using more of the exergy available by the gas burner. Eleven binders of different chemical composition were tested. While weight loss temperatures reached up to 480 °C for some binders, most of the coatings showed a very low weight loss onset. The remaining porosities of the coatings with inorganic binders were good with values of up to 83 %. Nevertheless, none of the binders showed sufficient mechanical stability to be used in an adsorptive coating without further measures improving ad- and cohesion.

With a suitable binder identified the next step was to figure out what is the optimal coating. The focus was put on increasing power and efficiency of the coated adsorber. Preliminary tests had shown that under certain conditions it might be possible to increase the efficiency while maintaining a high power output. Five identical adsorbers were coated with different amounts of adsorbents and characterized in a test rig. The possibility of major increases in efficiency was shown. A power output of above 350 W could be maintained by the adsorbers while the adsorbent mass was increased by a factor of 7. A mass ratio of 1.04 kg_{HX}/kg_S was achieved for the best adsorbers. Small scale samples with varying coating thicknesses were fabricated and characterized to study the observed effects in detail. Results from small scale samples and full scale adsorbers show a limitation in the heat transfer between metal and the adsorbent layer under these conditions. At more challenging conditions the mass transport is the limiting resistance.

After identification of the best binder and coating configuration the coating process itself was optimized. Twelve different rheology additives were tested to control the rheology of the coating slurry, a critical parameter for process optimization. Their influence on the viscosity, thermal stability and porosity of the coatings was characterized. The inorganic additives

showed no decomposition up to 500 °C and very good porosities while all organic based additives were ruled out because of their insufficient thermal stability. Their influence on the slurry viscosity has been thoroughly characterized including the influence of parameters such as shear rate, temperature, water content, the slurries yield stress and its thixotropic behavior. Optigel WH was chosen as the additive to control the slurry rheology in full scale applications.

Several adsorbents were identified for which the slurry can be prepared without ultrasonic deagglomeration. This facilitates large scale production processes and saves time, equipment and labor. It was shown that here the particle size distribution here is not dependent on the supersonic deagglomeration step.

Supplementary to the dip coating process the spray coating technique was developed and implemented for several different adsorbents. This process is established in the coating industry and allows for easier plug-in into existing coating capabilities and thus an easy scale up from lab to industrial scale. For the manufacturing of detailed high resolution coatings, the feasibility of screen printing with adsorptive materials was demonstrated.

Summing up it can be stated, that the main coating challenges for the production of adsorptive coatings could be solved. A suitable binder has been identified, the optimal coating configuration has been found and the process was tailored to the specific needs of large scale industrial production.

4.1 Conclusion and outlook

Unfortunately the heat pump market changed in the time while this thesis was carried out. Three years ago it was expected that adsorption heat transformation will be part of a shift to more sustainable heating and cooling. Companies like manufacturers of heating appliances, car manufacturers and others were putting up money and effort into the development of this technology. Nevertheless the fast rise of sustainable power production together with major improvements in the field of compression heat pumps has changed the picture. Together with the low price of compression heat pumps these developments have made it less and less likely that the adsorption heat transformation technology will find widespread application apart from some niche markets. If power to gas technologies are developed that make it possible to store renewable surplus energy and, at the same time the existing gas infrastructure is used exclusively to store the produced gas adsorption heat pumps and cooling devices could play a role again. This would be in line with the efforts to achieve the 95 % carbon dioxide reduction compared to 1990 in 2050. If we make the assumption that, firstly, the produced gas stays mainly fossil and has the corresponding carbon dioxide footprint and secondly a gas adsorption heat pump has a product life time of 20 to 25 years, the timeframe to sell this product is only about 7 more years. Otherwise the technology would contradict the 2050 goal set by the

German government. Despite these challenges, the findings made during this work have laid the foundation for the use of adsorptive coatings in other applications. Possible areas are adsorptive dehumidification especially for low humidity applications and adsorptive coatings for high temperature catalytic applications or sensors. For example the results obtained together with the spray coating technique developed have been applied to coating of ten adsorbers for open dehumidification application and are used in a pilot project.

5.1 Coating

5.1.1 Substrates and pretreatment

5.1.1.1 Small scale

Sheets of AlMg3 ($50 \times 50 \times 2 \text{ mm}^3$ cross cut and impact test, $150 \times 50 \times 0.5 \text{ mm}^3$ bend test) were supplied by HSL Lasertechnik GmbH, and used without any further mechanical processing. A uniform surface finish was achieved by a standardized cleaning procedure consisting of dipping the sheets in a cleaning bath (8.55 %wt Surtec S140, 045 %wt Surtec 089 in water) for 5 min at 80 °C followed by an acidic bath (13 % nitric acid in water) at room temperature. After each cleaning bath, the sample sheets were rinsed with deionized water. Alternatively the surface finish was carried out by using a cleaning bath (3.00 %wt Hakupur 50-636, 0.30 %wt Netzmittel 351 in water) for 10 min and a surface finish (DECORRDAL AL 20-18, 1.5 %wt in water) at room temperature for 90 sec.

Cleaning solutions were obtained from SurTec International GmbH, and Chemische Werke Kluthe GmbH, nitric acid (65 %) from Carl Roth GmbH & Co. KG.

5.1.1.2 Full scale

Heat exchanger HX-1 to HX5

Full scale heat exchangers were supplied by an industrial partner. The heat exchangers were, flat tube heat exchangers ($305 \times 21 \times 223 \text{ mm}^3$, 1.43 L) with plain triangular fins. Each heat exchanger consisted of 22 lamella layers ($80 \mu \text{m}$ thickness, 0.659 m² overall lamella surface) and 21 micro channel flat tubes (1.8 mm thickness, 18 channels of 75 μm width). The volume of the cooling structure available for cooling was 0.94 L, the surface per volume in the coatable structure 0.85 m²/L.

Heat exchanger HX-A and HX-B

Heat exchangers were supplied by an industrial partner. The heat exchangers were flat tube heat exchangers $(300 \times 49.5 \times 121 \text{ mm}^3, 1.80 \text{ L})$ with louvered triangular fins. The heat exchangers consisted of 13 lamella layers (40 µm thickness, 1.67 m² overall lamella surface) and 11 micro channel flat tubes (2.2 mm thickness). The volume of the cooling structure available for cooling was 0.98 L, the surface per volume in the coatable structure 1.70 m²/L.

High surface area heat exchanger

The Heat exchanger was fabricated by IFAM Dresden together with Haugg Industriekühler GmbH. The heat exchanger $(339 \times 100 \times 97 \text{ mm}^3, 2.84 \text{ L})$ consisted of 4 flat tubes with 39 aluminum fiber blocks soldered to the flat tubes.

Heat exchanger for open dehumidification

Heat exchangers were supplied by an industrial partner. The heat exchangers $(25 \times 300 \times 250 \text{ mm}^3, 1.88 \text{ L})$ consisted of 8 copper tubes (distance 32 mm, outer diameter 12.7 mm, inner diameter 11.5 mm), with 100 fins of 100 µm thickness. The total surface of the fins was 0.524 m².

Heat exchangers were visually inspected for structural integrity and leak-tested. The heat exchangers were weighed and connections to the water circuit were sealed using a PE cap and a silicon seal.

Degreasing, cleaning and surface preconditioning was carried out in a cleaning solution using a supersonic cleaning bath (Hakupur 50-636, 3.0 %wt, Netzmittel 531, 0.3 %wt, 60 °C, 480 sec, 12 kHz). After a rinsing step in deionized water the heat exchangers surface was passivated in a solution of Kluthe Decordal Al 20-18 in deionized water (1.5 %wt, 22 °C, 90 sec). The heat exchanges were thoroughly rinsed and visually checked for a uniform wetting of the surface prior to the coating process.

Hakupur 50-636, Netzmittel 531 and Decordal Al 20-18 were supplied by Kluthe GmbH.

Overview

Table 5-1 compares the different heat exchangers regarding their construction, size and coatable surface area.

name	type	dimensions	specific surface	cooling
			area	volume
HX-1 to HX-5	flat tube, plain triangular fins	$305 \times 21 \times 223$ mm ³ , 1.43 L	0.85 m ² /L	0.94 L
HX-A, and -B	flat tube, lou- vered triangular fins	25 × 32.5 × 120 mm ³ , 0.98 L	1.70 m ² /	0.98 L
high sur- face area HX	flat tube, alu- minium fibres	339 × 100 × 97 mm ³ , 2.84 L	3.91 m ² /L (aluminum fibres)	1.61 L
open de- humidifi- cation	round copper tube, aluminum fin	25 × 300 × 250 mm ³ , 1.88 L	0.28 m ² /L	1.88 L

Table 5-1: Properties of the heat exchangers that were coated

5.1.2 Adsorbents

The following adsorbents were used in this work:

TiAPSO, a titanium exchanged SAPO-34 type adsorbent with chabazite structure. TiAPSO SCT-323 was obtained from Clariant AG.

CBV-300, a Y-type zeolite adsorbent with ammonium cations. CBV-300 was obtained from Zeolyst International.

Na-Y, a Y-type zeolite adsorbent with sodium cations. Na-Y was obtained from Chemiewerk Bad Köstritz GmbH.

SAPO-34, it is a chabazite type structure adsorbent with hydrogen cations. SAPO-34 AQSA-Z02 was produced by Mitsubishi cooperation.

AlFum is a metal organic framework consisting of Al-OH-Al chains connected by fumarate linkers. It was obtained from BASF.

CAU10-H, it is an aluminum based metal organic frame work with Isophthalic acid linkers. CAU-10 was synthesized in-house at Fraunhofer ISE.

5.1.3 Binders

The following binders were used this work

Silres® REN 50, Silres® REN 60, Silres® HK46, Silres® MSE100 and Silres® MP50E were obtained from Wacker Industries AG.

Silikophen® P40W, Silikopon® EW, Silikoftal® HTS/MPA, Silikophen® P80/MPA, Silikophen® AC900, Silikophen® AC1000 have been supplied by Evonik Industries AG. ES-QUIM R-750 was obtained from ESQUIM cooperation and Silixan W220 from Silixan cooperation. Dynasilan Sivo 140 was supplied by Evonik Industries AG. Disperal P2 was obtained by Sasol Germany GmbH, potassium silicate from Chemdiscount GmbH, Resbond 792, Resbond 793, and Resbond 795 were obtained from Polytec PT GmbH, LRC Binder from Zyp Coatings Inc and Ceramabind 644-S from Aremco Products Inc. Ecrothan® 4075 was supplied by Michelman.

Binder concentrations were 15% wt in regards to the coating dry mass if not stated otherwise.

5.1.4 Coating slurry preparation:

The coating slurries were prepared in different ways depending on the substances used:

5.1.4.1 Coating slurry for kinetic test rig samples, cross cut test, impact test or adsorption measurements – without additives or catalyst.

Adsorbent was filled in a glass beaker and the dispersion medium according to Table 3-1 was added carefully to the adsorbent while stirring. The resulting dispersion was homogenized and treated with ultrasound (45 kHz, 5 min) for deagglomeration. Then the binder was added and the mixture was homogenized by stirring with a magnetic stirrer – the mixture was then used to coat the sample without further delay.

5.1.4.2 Coating slurry for kinetic test rig samples, cross cut test, impact test or adsorption measurements with catalyst, without additives.

Adsorbent was filled in an appropriate glass beaker and the dispersion medium was added carefully to the adsorbent while stirring. The resulting dispersion was homogenized and treated with ultrasound (45 kHz, 5 min) for deagglomeration for 5 min. Then the binder was added and the mixture was homogenized by stirring with a magnetic stirrer – the catalyst was added to the mixture, the mixture was homogenized again and then used to coat the sample without further delay.

5.1.4.3 Coating slurry for kinetic test rig samples, cross cut test, impact test or adsorption measurements with liquid additives.

Adsorbent was filled in an appropriate glass beaker. The additive was added to the dispersion medium and homogenized under continuous stirring. The dispersion-additive mixture was then added carefully to the adsorbent while stirring. The resulting dispersion was homogenized and treated with ultrasound (45 kHz, 5 min) for deagglomeration. The binder was added and the mixture was homogenized by stirring with a magnetic stirrer. It was then used to coat the sample without further delay.

5.1.4.4 Coating slurry for kinetic test rig samples, cross cut test, impact test or adsorption measurements with solid additives.

Adsorbent was filled in an appropriate glass beaker, the additive added and the mixture homogenized. The dispersion medium was added carefully to the adsorbent-additive while stirring. The resulting dispersion was homogenized and treated with ultrasound (45 kHz, 5 min) for deagglomeration. The binder was added and the mixture was homogenized again by stirring – the mixture was then used to coat the sample without further delay.

For stirring a Heidolph MR Hei-Standard magnetic stirrer was used. For deagglomeration a VWR USC200TH Ultrasonic cleaner (60 W, 45 kHz, 5 min, 1.8 L) was used. Dispersion medium xylene was a technical grade mixture of isomers used as received from VWR International GmbH. Dispersion medium acetone, technical grade was supplied by Deffner & Johann GmbH and used as received.

5.1.4.5 Coating slurry for full scale adsorbers

The dispersion medium was filled in an appropriate Gastronorm stainless steel container. The adsorbent was mixed with any solid additives if by manual stirring and added slowly to the dispersion medium, water, under continuous stirring. The resulting dispersion was homogenized and treated with ultrasound (45 kHz, 10 min) for deagglomeration. Then the binder was added and the mixture was homogenized by stirring. The mixture was then used to coat the sample. In case of multiple coatings the mixture was stirred in between the coating steps to keep the adsorbent particles suspended in the slurry and to prevent reagglomeration of the particles.

Two KPG stirrers with a PTFE coated steel shaft and head were used to stir the coating slurry. For deagglomeration an Elmasonic X-tra basic 800 cleaning bath (4000 W, 45 kHz, 70 L) was used.

The coating slurry

5.1.4.6 Screen printing slurry

Na-Y was mixed with the rheology additives HDK T30 and Optigel WH in powdered form. Water, the Ecrothan 4075 EM binder and the dispersion additive Tego Dispers 757E were added to the mixture and stirred well. The resulting paste was homogenized using a three roller mill.

Relative contents of substances in the coating slurry for the silicone and inorganic binders and for the coating slurries of the full scale adsorbers are giving in the following tables. If other compositions have been used for special reasons it is stated in the results section.

Binder	adsorbent	dispersion medium	binder
-	[%wt]	[%wt]	[%wt]
Silikophen® P40W	30	65	5
Silikopon® EW	23	73	4
Silikoftal® HTS/MPA	23	73	4
Silres® REN 50	23	73	4
Silres® REN 60	23	73	4
Silres® HK46	23	73	4
Silikophen® P80/MPA	24	72	4
Silikophen® AC900	24	72	4
Silikophen® AC1000	24	72	4
Silres® MSE100	24	72	4
Silres® MP50 E	30	65	5
ESQUIM R-750	30	65	5
Silixan W220	31	63	6

Ta	ble	5-2:	Slurry	composit	ion for	silicone	binders
			•/				

Binder	adsorbent	dispersion medium	binder
-	[%wt]	[%wt]	[%wt]
Sivo 140	37	56	7
Silres® Ren 50	29	66	5
Silres® Ren 60	27	68	5
Silres® HK 46	34	60	6
Sasol Disperal P2	70	18	12
potassium silicate	27	68	5
Resbond 792	28	67	5
Resbond 793	31	63	6
Resbond 795	16	81	3
LRC Binder	31	64	5
Ceramabind 644-S	27	68	5

Table 5-3: Slurry composition for inorganic binders

Table 5-4: Slurry composition for the full scale adsorbers

adsorber	adsorbent	dispersion medium	binder	rheology additive
-	[%wt]	[%wt]	[%wt]	[%wt]
HX-1 to HX-5	41	52	7	0.00
HX-A	34	63	4	0.00
HX-B	33	62	4	1.09
metal fiber	34	63	4	0.00
spray coating	36	58	6	0.30

5.1.5 Coating techniques

5.1.5.1 Coating of kinetic test rig samples, cross cut test, impact test or adsorption measurement samples

Dip coating technique

After cleaning the aluminum sheets, experiment numbers were engraved and the weight of the uncoated aluminum sheet was recorded. A self-adhesive stencil mask was applied to the alu-

minum sheets side to cover the parts that should be left free of coating. The stencil allows coating a defined surface. Two of these aluminum sample sheets were attached together back to back with custom made self-adhesive stencils. This was done to keep the backside of the sample free from coating slurry. The sample were then submerged in the coating slurry, left in the slurry at least 3 seconds and then slowly and steadily withdrawn of the slurry. The excessive slurry was drained and the sample dried while suspended for at least 12 h. The self-adhesive stencils were removed and the samples were cured at room temperature or in a muffle furnace. The dry weight of the adsorbent on the sample was determined by placing the sample in a vacuum drying cabinet, letting the sample desorb for 12 h and weighing the desorbed sample. For multilayer coating the samples were dried using a heat gun and then recoated until the desired coating thickness or adsorbent weight was achieved.

Spray coating technique

Cleaning, labeling, weighing and stenciling were carried out as for the dip coating technique. The coating slurry was filtered through a 125 μ m sieve to prevent the spray gun from clogging. The slurry was sprayed on the sample using a HVLP spray gun. For multilayer coatings the samples were dried in a muffle furnace at 80 °C and recoated until the desired coating thickness or adsorbent weight was achieved. The sample was dried to the touch and the selfadhesive stencils removed. The samples were cured in a muffle furnace and the dry weight of the adsorbent on the sample was determined by placing the sample in a vacuum drying cabinet, letting the sample desorb for 12 h and weighing the desorbed sample

Pipette technique

Cleaning, labeling, weighing and stenciling were carried out as for the dip coating technique. In preliminary tests correlation of slurry mass to final coating thickness was determined for the slurry and the slurry samples. The predetermined amount of slurry was dispensed on the sample and spread on the sample using a pipette. The sample was dried for at least 12 h and the self-adhesive stencils removed. The samples were cured at room temperature or in a muf-fle furnace and if applicable the dry weight of the adsorbent on the sample was determined by placing the sample in a vacuum drying cabinet, letting the sample desorb for 12 h and weighing the desorbed sample

5.1.5.2 Coating of full scale adsorbers

Dip coating technique

The heat exchangers to be coated were cleaned and the slurry was prepared as described before. All hydraulic connections were sealed to prevent the intrusion of coating slurry during the dip coating process. The slurry was transferred in a container that would fit the heat exchangers dimensions. The cleaned and dry heat exchanger was submerged in the coating slurry while it was ensured that no air is trapped in the heat exchanger structure. The heat exchanger was then manually withdrawn from the coating slurry at constant speed. Excess slurry was first drained and then removed with pressurized air using an Eputec Full Flow Airknife (61 cm). The coated heat exchanger was put in an oven (80 °C, 15 min) for drying. The heat exchanger coating was moistened by spraying water on the coating to prevent adsorption of water from the slurry into the coating layer. These coating steps were repeated until the desired coating mass was achieved. The coated heat exchanger was then dried, sealing of the hydraulic connections was and excess coating on parts not to be coated was removed and the coating was cured in the oven. The weight of the heat exchanger was determined prior to and after coating. The adsorbent dry mass was determined by weighing the adsorber at 200 °C.

Spray coating technique

The coating slurry was filtered through a 125 μ m sieve to prevent the spray gun from clogging. All hydraulic connections were sealed to prevent the intrusion of coating slurry during the dip coating process. The slurry was then sprayed on the dry heat exchanger using a HVLP spray gun. The coated heat exchanger was put in an oven (80 °C, 15 min) for drying. These coating steps were repeated until the desired coating mass was achieved. The coated heat exchanger was then dried, sealing of the hydraulic connections and excess coating on parts not to be coated was removed and the coating was cured in the oven. The weight of the heat exchanger was determined prior to and after coating. The adsorbent dry mass was determined by weighing the adsorber at 200 °C.

Screen printing technique

Aluminum foil as a substrate was fixed on a screen printing table. The paste was put on a screen printing frame (T55 type sieve, supplied by Johannes Gerstaecker Verlag GmbH) and worked into the sieve by doctor blading once with a plastic squeegee. The printing was carried out manually.

5.2 Porosimetry

Nitrogen sorption isotherms were measured with a Quantachrome NOVA 4000e or QuadraSorb SI with a Masterprep degassing unit. Samples were prepared from the cured coating and dried at 120 °C at decreased pressure for 1 day prior to the measurement. The specific surface area was calculated by applying the Brunauer–Emmet–Teller (BET) theory; the lower limit of the relative pressure was derived from the corresponding Rouquerol Plot. The upper pressure limit was held constant at p/p0 = 0.5. Pore volume was calculated according to the Gurvich Rule at the maximum of p/p0.

Water isotherms were measured on a Quantachrome Instruments Autosorb with vapor option or Quantachrome Instruments V Star 4 after vacuum degassing (120 °C/24 h).

5.3.1 Bend test

Bend tests were performed on a BYK cylindrical mandrel bend tester according to ISO 1519:2011. The coated sheets were bent with a curvature radius of 32, 16, 8 and 4 mm. The coating was visually inspected for cracks. The radius, at which the first failure was observed, was reported.

5.3.2 Cross cut test

Cross-cut tests were performed by cutting a grid of 6×6 orthogonal lines with 2 mm spacings. The equipment used was a Pro NT-cutting knife and a MFS 3000 multi-functional plate as stencil. Both were supplied by mtv messtechnik. Chipped-off coating particles were removed by gentle blowing with compressed air and the area was visually inspected. A cross cut rating was assigned according to ISO 2409:201 – ranging from 0 for an intact coating to 5 for a coating peeling off completely. A distinction was drawn between cohesion failure, where the fracture occured in the coating layer between single adsorbent particles and adhesion failure, where the point of failure was located at the substrate-coating interface.

5.3.3 Impact test

Impact tests were performed using a mtv mess-technik IP3000 impact tester. The falling weight (m = 1.00 kg) with a 20 mm diameter ball tip was dropped on the backside of the coated sheets to induce a shock like stress. Dropping heights of 10, 25 and 50 mm correspond to impact energies of 9.81 mJ, 24.53 mJ and 49.05 mJ respectively. The coating was visually inspected for cracks and the first height for which a fracture of the coating could be observed was reported.

For an easier comparison of the rating in the three different mechanical testing methods, all results were transformed into a score ranging from 0 for the most damaged and 3 for the least damaged. Table 5-5 shows the possible test out-comes and their respective scores.

hand test radius [mm]	non failing	1	8	16	32	
benu test radius [mm]	non tannig	4	0	10	52	
score	3	2.25	2.5	0.75	0	
cross cut test result	0	1	2	3	4	5
score	3	2.4	1.8	1.2	0.6	0
impact energy [mJ]	non failing	49.05	24.53	9.81		
score	3	2	1	0		

 Table 5-5: Relation between mechanical stability test results and their respective comparative scores.

5.3.4 Pull off tests

Two sheets of AlMg3 ($50 \times 50 \times 2 \text{ mm}^3$) where cleaned as described in chapter 5.1.1.1. A coating slurry was prepared as described above and spread on the sample sheets. The sheets were joined and dried. After drying two aluminum handles were glued to the samples using a custom made alignment rack. The glue was left to dry and the samples were tested in a Zwick Roell Z010 tensile testing machine.

5.3.5 Tape adhesion test

A self-adhesive tape (Tesafix 4965, 9 mm width) was fixed to the adsorbent sample and the pulled off with a speed of 50 mm/min maintaining an angle of 90°. A custom made "Abzug-sanlage Frolyt" testing apparatus was used. Since this test was only available in the later stage of the work it was not for the extensive binder testing.

5.3.6 Thickness measurement

Thickness measurements were carried out using the eddy current method. Thickness measurements were averaged over 5 points on the sample.

5.4 Thermal characterization

5.4.1 Thermal gravimetrical analysis

The thermal decomposition of the pure binders was characterized by TGA using a Setaram Setsys Evolution 1600. Samples were prepared from the binders using the curing conditions listed in chapter 3.1.2.1 and 3.1.2.2. Rheology additive samples were prepared using CBV-300 as adsorbent, Silres® MP50E as binder and cured at 200 °C. The cured binder samples were then placed in an aluminum crucible (diameter = 6.2 mm, height = 3 mm) and heated from 40 °C to 500 °C at a rate of 5 K/min and were held at 500 °C for 30 min before cooling down to room temperature. The onset of the thermal decomposition was determined accord-

ing to ISO 11358:1997 as the intersection of the baseline and the inflection tangent, compare figure 5.1.



Figure 5.1: Schematic of onset point determination – the onset point corresponds to the intersection of the two lines.

Higher resolution measurements were carried out on a TA Instruments TGA 5500. Here the temperature ramp is regulated according to the actual weight loss. The onset of the thermal decomposition was determined according to ISO 11358:1997.

For a fast measurement of weight loss a moisture analyzer was used in a screening tests of the rheology additives. A small amount of sample was placed in the aluminum crucible and heated to 200 °C for 90 min. The maximal weight loss was recorded. The weight loss relative to dry mass (τ) was calculated from the weightloss (∂), the concentration of solvents in the product (c_{slv}) and the dry mass in the additive (ϕ) according to formula (18).

$$\tau = \frac{(\partial - c_{slv})}{\varphi} \cdot 100\% \tag{18}$$

5.4.2 Temperature controlled diffuse reflection infrared Fourier transform spectroscopy

Temperature controlled diffuse reflection infrared Fourier transform spectroscopy (T-DRIFTS) measurements were carried out on a Perkin Elmer Frontier FT-IR spectrometer coupled with a Pike Technologies Diffuse IR heat chamber. The samples were heated from 40 °C to 700 °C at a rate of 2 K/min. Spectra were measured every 2 min, which gives a resolution of 2 °C/spectrum.

Temperature dependent X-Ray diffraction patterns were measured using a Bruder D8 Advance diffractometer with DaVinci[™] design. Cu-Ka radiation from a Cu anode tube at 40 kV/40 mA and a Ni Filter in Bragg Brentano geometry was used in the experiment. An MTC-LOWTEMP heating chamber was used.

5.5 Rheology characterization

Rheology measurements were carried out using an Anton Paar MCR 502 Rheometer and a disposable measurement geometry consisting of a measurement shaft D-CP /PP7, the measurement plate D-PP25Al/S07 and a disposable dish EMS/TEK500/600. Temperature was set at 15 °C if not stated otherwise.

All liquid rheology additives where predispersed in the water before the adsorbent was added. Solid additives were mixed with the adsorbent before dispering in the water. All additive concentrations refer to the whole slurry weight. Additive concentrations for the inorganic additives are stated for the respective measurements. Concentrations of the organic additives were chosen as follows: TEGO ViscoPlus 3060: 1.00 %wt, Borchi Gel 0621: 3.00 %wt, Tafigel Pur 60: 2.00 %wt, Rheovis AS: 3,50 %wt, Tafigel AP 30: 0,75 %wt, BYK D420: 1,50 %wt.

5.5.1 Measurement profiles

5.5.1.1 Rheology as a function of shearrate

The sample was placed into the measurement geometry, the measurement gap was set to a value between 500 μ m and 1000 μ m and the excess slurry was removed. The sample was let rest for 30 s and then measured using a logarithmic shear rate ramp from 0.03 to 1000 s⁻¹ with 61 points and a sampling time of 5 s. For samples that showed transient effects in the shear rate range from 0.03 to 0.1 s⁻¹ was measured using a logarithmic shear rate ramp with 8 points and a sampling time of 15 s.

5.5.1.2 Influence of temperature on viscosity

The temperature of the measurement geometry was set to the temperature of the measurement and let equilibrate. The sample was placed into the measurement geometry, the measurement gap was set to a value between 500 μ m and 1000 μ m and the excess slurry was removed. The sample was let rest for 30 s and then measured using a logarithmic shear rate ramp from 0.03 to 1000 s⁻¹ with 61 points and a sampling time of 5 s. The measurement in the shear rate range from 0.03 to 0.1 s⁻¹ was measured using a logarithmic shear rate ramp with 8 points and a sampling time of 15 s.

5.5.1.3 Temperature Ramp

The temperature of the measurement geometry was set to 20 °C and let equilibrate. The sample was placed into the measurement geometry, the measurement gap was set to a value between 500 μ m and 1000 μ m and the excess slurry was removed. The sample was let rest for 10 s and then measured at a shear rate of 0.1, 1 and 10 s⁻¹ with 20 measurement points and a sampling time of 10, 5 and 5 s respectively. The temperature was raised from 20 to 50 °C heating at rate of 0.3 K/s.

5.5.1.4 Yield point shear stress method

The sample was placed into the measurement geometry, the measurement gap was set to $300 \,\mu\text{m}$ and the excess slurry was removed. The sample was let rest for 30 s and then measured using a logarithmic shear rate ramp from 0.1 to 1 s⁻¹ with 3 points and a sampling time of 30 s, followed by a logarithmic shear rate ramp from 1 to 10 s⁻¹ with 5 points and a sampling time of 10 s, followed by a logarithmic shear rate ramp from 10 to 50 s⁻¹ with 5 points and a sampling time of 2 s. The resulting shear stress was measured. The measurement data was fitted to the Herschel Bulkley model using R version 3.4.0.

5.5.1.5 Yield point deformation method

The sample was placed into the measurement geometry, the measurement gap was set to $300 \,\mu\text{m}$ and the excess slurry was removed. The sample was let rest for 30 s and then measured using a linear shear stress ramp from 1 to 100 Pa with 200 measurement points and a sampling time of 1 s. The resulting deformation of the slurry was measured.

5.5.1.6 Thixotrophy

The sample was placed into the measurement geometry, the measurement gap was set to $300 \ \mu\text{m}$ and the excess slurry was removed. In a first measurement the samples linear viscous elastic region was determined by an deformation sweep measurement. In a second measurement with a new sample the sample was let rest for 30 s and then characterized at low shear stress using a rotational measurement with a deformation of 1 % and a frequency of 10 s⁻¹ for 100 s. The storage and loss module were recorded. The sample was then subjected to high shear stress with a rotational measurement at 500 s⁻¹ for 5 s, the samples relaxation was characterized at low shear stress with a rotational measurement, a deformation of 1 % and a frequency of 10 s⁻¹ for 100 s.

For the rotatory measurement the sample was placed into the measurement geometry, the measurement gap was set to 300 μ m and the excess slurry was removed. The samples viscosity was then determined by a measurement step with a shear ate of 0.2 s⁻¹ for 50 s, a measurement step with a shear rate of 500 s⁻¹ for 2 s and a measurement step with a shear rate of 0.2 s⁻¹ for 2.0 s.

5.6 Particle Size

Particle Size distributions was determined using a Beckmann Coulter LS 13320 Laser Diffraction Particle Size Analyzer. The Fraunhofer model with a refractory index real part of 1.332 for the liquid and 1.4 for the solid part with an imaginary part of 0.1 was used. For the measurements with mega sonic deagglomeration the samples were dispersed in water and subjected to mega sonic treatment (1MHz, 5 min) in a Sonosys[®] MGH Series Generator.

5.7 Density measurements

5.7.1 Density of coating

The coating thickness was determined and the sample area was determined by geometrical consideration. The weight of the desorbed coating was determined and the density was calculated.

5.7.2 Density of coating block

The coating slurry was poured into a silicone mold, dried and cured. The resulting coating block was sanded into a cuboidal form. The dimensions were measured using a caliper and the volume was calculated. The weight of the desorbed coating was determined and the density calculated.

5.7.3 Density of pressed adsorbent tablets

Adsorbent was pressed into a tablet form using a GECHTER pneumatic aided manual toggle press and a cylindrical mold. Tablets were pressed with pressures of 8, 32, 56 and 80 MPa. The height of the tablet was determined using a caliper and the volume of the tablets was calculated. The weight of the desorbed adsorbent tablet was determined and the density was calculated.

5.7.4 Bulk density

The bulk density was determined by pouring the adsorbent in a graduated cylinder and shaking the sample until no further settling of the adsorbent could be observed. The volume of the adsorbent and its desorbed weight were determined and the bulk density was calculated.

5.8 Full scale adsorber characterisation – ADSEL Test

5.8.1 Test rig

Adsorption kinetics of the full scale adsorbers were characterized on a test rig as shown in Figure 5.2. A large pressure jump (LPJ) setup was used. In the test rig two separate chambers

were connected through a pneumatic valve - a primary chamber or measurement chamber and a secondary chamber or evaporator chamber. The primary chamber held the adsorber. It was attached to a high precision scale that recorded the weight change during the adsorption process. Taking into account all effects the weight measurement is can be assumed to have a precision of ± 2 g according to Wittstadt et al.¹²³ The adsorber was connected to a hydraulic circuit used to regulate its temperature. The water temperatures at the adsorbers inlet and outlet were measured. Together with the volume flow rate in the hydraulic circuit the temperatures was used to calculate the heat dissipated into the heat exchanger.



Figure 5.2: Schematic representation of the test setup used to characterize the coated full scale adsorbers with 1) primary chamber, 2) scale, 3) adsorber with hydraulic connections, 4) valve, 5) secondary chamber, 6) evaporator partially submerged in water.

5.8.2 Experimental procedure

Desorption of the adsorber was carried out using a vacuum pump (90 °C, 6 h) completely desorbing the adsorbent. The temperature of the adsorber was then set to adsorption temperature level T_m and the evaporator temperature to evaporation temperature level T_l . The target starting loading of the adsorber was set with a dosing device by incremental dosage of small amounts of water vapor from the evaporator chamber to the adsorber. Using equilibrium data and by taking into account the temperature triple $T_h / T_m / T_l$, the target starting pressure (p_{init}) and the corresponding starting loading of the adsorber (X_{min}) were calculated as shown in equation (19) and (20).

$$X_{\min} = X(T_H, p_{Sat}(T_m)).$$
(19)

$$p_{\text{init}} = p(X_{\min}, T_{\text{m}}). \tag{20}$$

The measurement was then started by opening the valve between evaporator and measurement chamber allowing free flow of the water vapor. The adsorption was measured over a fixed time of 2 hours. Further details concerning the measurement procedure are given in Wittstadt et al.¹²³

The measurement was subdivided into several single steps (index i) for analytical processing. An energy balance of the primary hydraulic loop with the temperature difference between adsorber inlet and outlet (ΔT_{pc}^{i}) , the volume flow of water through the adsorber (\dot{V}_{pc}^{i}) , the density of the water (ρ_{liq}^{i}) , its heat capacity $(c_{p,liq}^{i})$ and the duration of the measurement step (t^{i}) was used to calculate the adsorption power for each step (\dot{Q}_{Ads}^{i}) . Thermal losses to the environment were considered by using a correction term (\dot{Q}_{loss}^{i}) . For the adsorber evaluation a mean adsorption power was calculated according to equation (21). In this work the adsorption power was calculated for the time interval where 90 % of the adsorption had taken place.

$$\overline{\dot{Q}_{Ads}} = \frac{1}{n} \cdot \sum_{i=1}^{n} \left[\rho^{i}_{Fluid} \cdot c^{i}_{p,liq} \cdot \dot{V}^{i}_{pc} \cdot \Delta T^{i}_{pc} + \dot{Q}^{i}_{loss} \right]$$
(21)

5.9 Small scale sample characterization – kinetic test rig

126

Small scale samples have been characterized by using a volumetric adsorption dynamic test rig. The apparatus has been described in detail by Sapienza et al, a schematic drawing is shown in Figure 5.3.¹²⁴ The adsorption process was monitored by measuring the pressure change in a closed measurement chamber. Large pressure jump (LPJ) measurements were carried out by desorbing the sample to a desired initial loading, cooling it down to adsorption temperature. Then the sample was subjected to a water vapor atmosphere with a pressure corresponding to the water vapor pressure of T₁ so that the adsorbent layer adsorbed water until it was in equilibrium with the surrounding gas phase. The dropping pressure was measured and used to calculate the loading of the sample. The surface temperature evolution at the outer adsorbent layer was measured with an IR-sensor (Optris CT LT). Desorption was carried out at T = 95 °C and p = 23 mbar, adsorption at T = 35 °C and an initial pressure of p = 23 mbar.

For large temperature jump (LTJ) measurements the samples temperature and the surrounding water vapor atmosphere were controlled to set the samples preloading. The ad- or desorption is started by a temperature step function imposed by the hot/cold plate on the sample. The adsorption process was characterized by the recorded surface temperature and pressure change in the chamber. Desorption was carried out jumping from T = 68 to T = 95 °C with p = 66 mbar, adsorption jumping from T = 62 °C to T = 39 °C with p = 16 mbar. The characteristic time (t₉₀) is defined analogous to the full scale samples as the time it takes to complete 90 % of the adsorption process. A constant adsorption enthalpy (Δh_{Ads}) of 3200 kJ/kg, the time t₉₀ and the water ad- or desorbed (m_{H20,90}), which is calculated from the pressure signal were used to calculate the mean power.



Figure 5.3: Schematic drawing of the test rig with temperature controllable liquid water reservoir (1), dosing chamber (2), temperature controlled housing (3), vacuum pump for evacuation at desorption (4), cold/hot plate (5), sample (6), measurement chamber (7) and temperature control unit for the hot/cold plate (8).

6 List of Figures

Figure	1.1: Schematic representation of adsorption with 1) adsorptive, 2) adsorbate 3) adsorbent, 4) adsorption and 5) desorption
Figure	1.2: adsorption process (left) with a low temperature level heat source (1), a reservoir of adsorptive e.g. water (2), evaporator (3), adsorber (4) and middle temperature level heat sink (5); desorption process (right) with middle temperature level heat sink (1), condensator (3), adsorber (4) and high temperature level heat source (5)
Figure	1.3: Different shapes of adsorbent for heat transfer - pellets or granules (left), monolith (middle) and coating (right)
Figure	1.4: Different possibilities of contacting the adsorbent to heat exchanger: granular pellets filled into the adsorber, the fixed bed configuration (left), complete filling of the lamellas the so called consolidated bed (middle) and a coating (right)5
Figure	1.5: chemical structure of an inorganic binder - aluminium oxide (corundum) - aluminium in grey and oxygen in white (left), an organic binder – polyacrylate (middle) and a hybrid binder silicone (right)
Figure	1.6: Schematic of polymer molecule chains film forming (top right) and crosslinking (bottom right)
Figure	1.7: Hydrolization of a silicone oligomer and condensation reaction crosslinking the oligomers
Figure	1.8: Cohesion failure (left) and adhesion failure (right) in a coating11
Figure	1.9: Cylindrical mandrel bending test (left), impact test (middle) cross cut test (top right), tape adhesion test (bottom right)
Figure	1.10: Model for the mathematical description of viscosity
Figure	1.11: Different shear rate dependent behaviours of liquids (left) and yield point for a bingham fluid with the yield point as the y intercept
Figure	1.12: Deformation as a function of the shear stress for yield point determination.16
Figure	1.13: Time dependent viscosities of liquids shear stress with the resulting viscosity (left), and a oscillatory-rotatory-oscillator measurement profile
Figure	1.14: Measurement profile for a rotatory thixotropy measurement
Figure	1.15: Fumed silica network breaking (top), bentonite house of cards structure (bottom left) and reoriantation because of flow (bottom right)
Figure	1.16: Isosteric diagram of the heat pump process, isosteres are depicted as dashed lines the process as red arrows
Figure	1.17: Heat and mass transfer in the coating layer with coating (1), metal substrate (2), fluid (3) and mass transport in the gas phase (a), mass transport in the coating layer (b), heat transport through the coating layer (c), heat transfer from the coating layer tot he metall substrate (d), heat transport through the metall substrate (e), heat transfer from the metall substrate to the fluid (f)
Figure	3.1: Cross cut test specimen (left), cylindrical mandrel bending test specimen (middle) and impact test testing apparatus (right)

Figure	3.2: Tape adhesion test measurement - force needed for the detachment of a coating with a width of a 9 mm, moving average over 10 values
Figure	3.3: Normalized weightloss of the pure binder and the binder in the coating calculated by substracting the adsorbents weightloss due to desorption from the overall coatings weightloss
Figure	3.4: BET surface area (red) and pore volume (turqouise) for the investigated coatings (columns) and the pure adsorbent (dashed line)
Figure	3.5: cumulative pore volume (left) and its derivative (right) for an slightly blocked Silres® MP50 E and a severely blocked Silikophen® P40W coating
Figure	3.6: Water isotherms of Silres® MP50E coating and the pure adsorbent
Figure	3.7: Thermogravimetric analysis of the different silcone binders – weight loss as a function of temperature
Figure	3.8: T-DRIFTS measurement of the Silres® MSE100 binder, IR Spectra on the y axis, intensity is color coded
Figure	3.9: T-Drift measurement of the Silikophen® AC900 binder, IR Spectra on the y axis, intensity is color coded
Figure	3.10: T-DRIFTS measurement of the Silikophen® AC1000, IR Spectra on the y axis, intensity is color coded
Figure	3.11: Comparison of the mechanical stability of coatings with different binders, bending test (black), cross cut test (turquoise) and impact test (red)
Figure	3.12: Cohesion failure of the ESQUIM R-750 binder51
Figure	3.13: Silres® MP50 E based coating after tempering at 500 °C for 300 min 52
Figure	3.14: Silicone resin reacting to silicon oxide
Figure	3.15: In situ temperature dependend X-ray diffraction pattern of Disperal P2 (shifteted by 10 a.u. for better comparisson). No structural change took place during the temperature treatment up to 200 °C
Figure	3.16: graphical representation of the remaining pore volume and BET surface area of the coatings with inorganic binders
Figure	3.17: Thermogravimetric analysis of the different inorganic binders – weight loss as a function of temperature
Figure	3.18: T-DRIFT measurements of the LRC binder at different temperatures58
Figure	3.19: Power output of the two identical adsorbers with different amounts of coatings
Figure	3.20: HX-1 to HX-5 from left to right
Figure	3.21: Decreasing pressure during adsorption for a LPJ measurement of the small scale samples
Figure	3.22: Course of surface temperature for SSc-1, the thinnest and SSc-4, the thickest small scale sample during a LPJ measurement
Figure	3.23: Pressure and relative loading as a function of time during LTJ adsorption.68
Figure	3.24: Pressure and relative loading as a function of time during LTJ desorption.69

Figure 3.25: schematic representation of heat and mass transfer in the experiment with 1) Coating layer, 2) aluminum substrate, 3) hot/cold plate, a) mass transfer in the gas phase, b) mass transfer in the coating layer, c) heat transfer in the coating layer, d) contact resistance coating layer – aluminum substrate, e) heat transfer in the aluminum substrate and f) contact resistance aluminum substrate – hot/cold plate	
Figure 3.26: Simulation results and experimental results compared to each other for large pressure jump measurements (top) and parameter variation of the heat transfer between adsorbent layer and aluminum sample plate (bottom)71	
Figure 3.27: Mass uptake and power output over time for the measurments at 90/35/10.73	
Figure 3.28: Mass uptake and power output over time for the measurments at 90/39/4.73	
Figure 3.29: Water uptake, adsorption time and power output as a function of the amount of adsorbent coated on the heat exchanger for measurements at 10/35/90 and 4/39/110 °C	
Figure 3.30: Schematic representation of the adsorber with 1) coating layer, 2) aluminium lamella, 3) aluminium flat tube and 4) fluid channel. Heat transfer is depicted on the right side in blue starting with heat conduction in the coating, heat transfer from coating to the lamella, heat conduction in the lamella, heat transfer at the soldered contact from lamella to flat tube, heat conduction in the flat tube and heat transfer from flat tube to fluid	
Figure 3.31: Coating and adsorbent densities measured with different methods78	
Figure 3.32:Weight loss relative to dry mass (turquoise) and weight loss (red) of rheological additives during heating in the moisture analyzer. For Tafigel AP 30 the weightloss relative to dry mass was below 0 %	
Figure 3.33: Thermogravimetric analysis of the inorganic rheology additives	
Figure 3.34: X-ray powder diffraction patterns for Optigel WX, Optgel WH and Bentone EW at 25 and 200 °C. Diffraction at 200 °C was shifted upwards for better comparability	
Figure 3.35: BET surface area (left) and pore volume (right) of the coatings using different additives – the value for the pure adsorbent is shown as a dashed line.85	
Figure 3.36: Water isotherems of pure adsorbent and of a coating with rheology additive, corrected for binder and additive content	
Figure 3.37: scratched measurement plate (left), transient effects (middle) and artefacts because of drying coating (right)	
Figure 3.38: Slurry rheology of slurries with different additives	
Figure 3.39: Concentration dependend shear thinning effects for temperature stable inorganic additives	
Figure 3.40: Concentration dependend shear thinning effects for temperature stable fumed silica additives90	
Figure 3.41: Shearrate dependend viscosity for different temperatures, temperature dependend visoscosity at different shearrates and shearrate dependend viscosity for different water contents	

Figure	3.42: stress ramp for yield stress determination – no distinct slope change can be observed (left). Shear stress as a function of shear rate for the determination of the yield stress (right)
Figure	3.43: Viscosity as a response to a shear stress step function and the following recuperation of viscosity
Figure	3.44: Young modulus for an ORO measurement to characterize the slurry thixotrophy
Figure	3.45: Particle size distribution of different adsorbent with and without deagglomeration, log-scale x achsis
Figure	3.46: Drawing of the high surface area adsorber with flat tubes at the sides sandwiching the fiber metal pieces (left), cross cut through a coated piece of coated metal fibers showing the accessibility of the structure for the slurry penetration in dip coating (middle) and image of a position at which the coating complicates gas access to the inner part of the adsorber (right)
Figure	3.47: Mass uptake and power output of the metal fiber adsorber during large pressure jump measurements at temperatures of 90/35/10 °C, up to a time of 750 s
Figure	3.48: Blocked fins in a dip coated adsorber100
Figure	3.49: Close up of a spray coated adsorber (left) and principle of open air dehumidification (right)
Figure	3.50: Measurement results of air humidity, air temperature and water temperature for the spray coated adsorbers
Figure	3.51: Shear rate dependent viscosity of the coating slurry at the start and end of the spray coating process
Figure	3.52: Test print at IFAM Dresden, pinholes and foam bubbles are discernable (left and middle). Test print at Fraunhofer ISE (right)
Figure	3.53: Rheological Profile, of commercial screen printing paste and the screen printing paste using Na-Y zeolite – with and without homogenization in a three roller mill
Figure	5.1: Schematic of onset point determination – the onset point corresponds to the intersection of the two lines
Figure	5.2: Schematic representation of the test setup used to characterize the coated full scale adsorbers with 1) primary chamber, 2) scale, 3) adsorber with hydraulic connections, 4) valve, 5) secondary chamber, 6) evaporator partially submerged in water
Figure	5.3: Schematic drawing of the test rig with temperature controllable liquid water reservoir (1), dosing chamber (2), temperature controlled housing (3), vacuum pump for evacuation at desorption (4), cold/hot plate (5), sample (6), measurement chamber (7) and temperature control unit for the hot/cold plate (8).

7 List of Tables

Table 1-1: Viscosity values of common substances at 20 °C ⁵²	14
Table 1-2: Process steps encountered in the coating process and their correspondences rates ⁵²	nding shear
Table 2-1: Overview of binders for adsorptive coatings used in literature	29
Table 3-1: List of binders, their chemical composition, dispersion media and c temperatures used	curing 39
Table 3-2: BET surface area value, pore volume and the corresponding pressu	re41
Table 3-3 : Onset temperatures for weight loss during TGA	44
Table 3-4: Results of the mechanical testing - cross cut rating and the correspondence failure mode, failing diameters for the bending test and failing impact of the impact test.	onding energies for 49
Table 3-5: List of binders, their curing temperatures and chemical composition	n53
Table 3-6: BET surface area, pore volume and the corresponding pressure for coatings with inorganic binders	the 55
Table 3-7: Thermogravimetric analysis onset temperatures for the inorganic bi	inders56
Table 3-8: Results of the mechanical testing - cross cut rating and the correspondence failure mode, failing diameters for the bending test and failing impact of the impact test.	onding energies for 59
Table 3-9: Coated heat exchangers and their properties	60
Table 3-10: Properties of the coated small scale samples	62
Table 3-11: Properties of the heat exchangers coated	62
Table 3-12: Sorbent mass, mass ratio and fill factor of the coated adsorbers	
Table 3-13: Slope of the decreasing pressure in the first part of the measureme	ent 64
Table 3-14: Measurement results for large pressure jump adsorption and large temperature jump de- and adsorption measurements of small scale same	ples 67
Table 3-15: Measurement results for the full-scale adsorbers	72
Table 3-16: Densities of adsorbents and their coatings determined with differe	nt methods
Table 3-17: Rheology additives to be tested, their supplier and chemical type.	79
Table 3-18: Rheology additives with their weight loss during heating to 200°C screening procedure and where applicable the maximum water content to the supplier	c in the according
Table 3-19: BET surface area and total pore volume of coatings with different additives	rheology 84
Table 3-20: Results for the coated heat exchanger	

Table 5-1: Properties of the heat exchangers that were coated	112
Table 5-2: Slurry composition for silicone binders	115
Table 5-3: Slurry composition for inorganic binders	116
Table 5-4: Slurry composition for the full scale adsorbers	116
Table 5-5: Relation between mechanical stability test results and their respective comparative scores.	120

8 Abbreviations

%wt	percent weight
Q _{Ads}	adsorption power
Q ⁱ _{Ads}	adsorption power for each step
\dot{Q}^i_{loss}	Thermal losses to the environment
\dot{V}^{i}_{pc}	volume flow of water through the adsorber
T fluid	logarithmic mean fluid temperature
C ⁱ p,liq	heat capacity water
t ⁱ	duration of the measurement step
ΔT^{i}_{pc}	temperature difference between adsorber inlet and outlet
$ ho_{liq}^{i}$	density of the water
T _s	sorbent temperature
T _{inlet}	water temperature at inlet
T _{outlet}	water temperature at outlet
Ϋ́	shear rate
∂	weightloss, partial derivative
°C	degrees celsisus
μm	micrometer
A	area
a.i.	abosorbance intensity of T-DRIFT measurement
ADSEL	adsorber element
AlFum	Aluminum Fumarate
AlMg3	aluminium alloy
a.u.	arbitrary units
ASTM	American Society for Testing and Materials
BET	Brunauer–Emmet–Teller
cat	catalyst
CAU-10H	Aluminium isophthalate
-----------------	---
CBV-300	Y type zeolite, NH3 exchanged
c	centi
CO ₂	carbon dioxide
СОР	coefficient of performance
cp	specific heat capacities
Cslv	solvent concentration
Cu-Ka	copper K alpha radiation
d	particle radius
d	diamter
DDZ70	zeolite Y
EER	energy efficiency ratio
et al.	et alii / et aliae / et alia
EU	united states of europa
F	force
FT-IR	infrared Fourier transform spectroscopy
g	gravitational acceleration
g	gramm
g	starting pressure
GC-MS	gas chromatography – mass spectroscopy
GK	Gitterschnitklasse
h	film thickness
h	hour
H2O	water
H2O	water
hcond	specific condensation enthalpy
HP	heat pump
hads	specific adsorption enthalpy
HVLP	high volume low pressure

HX	heat exchanger
IFAM	Institut für Fertigungstechnik und Angewandte Materialforschung
ISE	Institut für Solare Energiesysteme
ISO	international organization for standardization
К	consistency index
K	Kelvin
k	thermal conductivity
g	gram
Hz	frequency
k	kilo (10 ³)
V	volt
L	liter
LPJ	large pressure jump
LTJ	large temperature jump
m	mass
m	meter
Α	ampere
MHz	mega hertz
min	minutes
m	milli (10 ⁻³)
J	joule
m	meters
MPa	mega pascale
ms	adsorbent mass
n	shear thinning index
Ν	newton
Na-Y	zeolite Y, sodium cation
Ni	nickel
NO _x	nitrogen oxide in different oxidation states
	1

ORO	oscillatory-rotational-oscillatory
ORO	oscillatory rotatory oscillatory
р	pressure
Р	power
Pa	pascale
Pads	adsorber power output
PEG	Polyethylene glycol
PTFE	polytetrafluoroethylene
PU	Polyurethane
PVA	polyvinylic alcohol
QAds	Adsorption energy
Qcond	condensation energy
Qcool	isosteric cooling of the adsorber
Qdes	desorption energy
Qheat	isosteric heating energy
r	ratio
R&D	research and development
RT	room temperature
S	seconds
S	sorbent
SAPO-34	silicon aluminium phosphate 34
SiO ₂	silicone oxide
SSc	small scale sample
t	time
t 90	time to complete 90 % of the adsorption process
t 90	time until 90% of equilibrium loading is reached
T-DRIFTS	temperature resolved diffuse reflectance infrared Fourier transform spectroscopy
TGA	thermogravimetric analysis
Тн	high temperature
	1

TiAPSO	titanium-aluminum-phosphorous-silicon-oxide
TL	low temperature
Тм	middle temperature
T-XRD	temperature resolved X-ray diffraction
U	velocity, withdrawal speed,
UA	product of heat transfer coefficient and area
US	united states of america
V	relative particle speed
W	watts
Xmin	starting loading
α	heat transfer coefficient
$\Delta \mathbf{h}_{ m Ads}$	adsorption enthalpy
ΔΤ	temperature difference
ΔΧ	water uptake
η	viscosity
θ	theta, diffraction angle
v	wavenumber
ρ	density
ρ	density
σ	shear stress
σ0	yield stress
τ0	yield stress
φ	dry mass in the additive
φ	fill factor
	ļ

9 List of publications

Peer-reviewed journal articles and book chapters

P. Bendix, S. K. Henninger, and H-M. Henning, Temperature and Mechanical Stabilities and Changes in Porosity of Silicone Binder Based Zeolite Coatings, *Ind. Eng. Chem. Res.*, 2016, 55 (17), pp 4942-4947, DOI: 10.1021/acs.iecr.6b00558

P. Bendix, G. Füldner, M. Möllers, H. Kummer, L. Schnabel, S. Henninger, H-M. Henning, Optimization of power density and metal-to-adsorbent weight ratio in coated adsorbers for adsorptive heat transformation applications, *Appl. Therm. Eng.*, **2017**, 124, pp 83-90, DOI: http://dx.doi.org/10.1016/j.applthermaleng.

D. Lenzen, P. Bendix, H. Reinsch, D. Fröhlich, H. Kummer, M. Möllers, P. Hügenell, R. Gläser, S. Henninger, N. Stock, Scalable Green Synthesis and Full-scale Test of the Metal-Organic Framework CAU-10-H for Use in Adsorption-Driven Chillers, *Adv. Mater.*, **2017**, 30, 06, DOI: 10.1002/adma.201705869

L. Schnabel, G. Füldner, A. Velte, E- Laurenz, P. Bendix, H. Kummer, U. Wittstadt, Innovative Adsorbent Heat Exchangers: Design and Evaluation, In: Bart H.-J., Scholl S. (eds) Innovative Heat Exchangers, Springer, Cham, DOI: 10.1007/978-3-319-71641-1_12

S. K. Henninger, S.-J. Ernst, L. Gordeeva, P. Bendix, D. Fröhlich, A. D. Grekova, L. Bonaccorsi, Y. Aristov, J. Jaenchen, New materials for adsorption heat transformation and storage, *Renew Energ*, **2017**, 110, pp 59-68

Talks and posters:

Poster: P. Bendix, H-M. Henning, S. Henninger, Characterization of mechanical performance of adsorbent coatings, Sorption Friends Conference, 14.-16.09.2015, Milazzo, Italy.

Poster: G. M. Munz, F. Jeremias, P. Bendix, H. Kummer, C. Bongs, H. Fugmann, T. Wolff, S. K. Henninger, Progress in Open Dehumidification: Formulation of Advanced. Adsorbents for Latest Generation Heat Exchangers, Sorption Friends Conference, 14.-16.09.2015, Milazzo, Italy.

Talk: P. Bendix; H. Henning; S. K. Henninger, Zeolite coatings by silicone binders - a thorough characterization, 28. Deutsche Zeolith-Tagung, 02.-04.03.2016, Giessen, Germany.

Talk: P. Bendix, G. Füldner, H-M. Henning, S. K. Henninger, H. Kummer, M. Möllers, Experimental assessment of performance and COP as a function of adsorbent to heat-exchangermass ratio, IMPRES Conference, 23.-26.10.2016, Taormina, Italy.

Talk: G. Füldner, P. Bendix, S. K. Henninger, M. Möllers L. Schnabel – Evaluation of Water adsorption in Binder based Adsorbent Coatings for the application in adsorption heat pumps, IMPRES Conference, 23.-26.10.2016, Taormina, Italy.

Poster: D. Lenzen, P. Bendix, D. Fröhlich, H. Reinsch, H. Kummer, C. Janiak, S. Henninger, N. Stock, Scalable green synthesis and full scale test of the Al-MOF CAU 10-H for use in adsorption driven chiller, 29. Deutsche Zeolith-Tagung, 01.-03.03.2017, Frankfurt Germany.

Talk: S.-J. Ernst, A. A. Narasoma, P. Bendix, A. Morgenstern, H.-J. Bart, S. K. Henninger, Simulation of Adsorbent coated Heat Exchangers for Dehumidification, Fachgruppentreffen Adsorpti on, 28.02.-02.03.2018, Kiel, Germany.

10 Eidesstattliche Versicherung

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Ort und Datum

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142

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Acknowledgements

As Sir Isaac Newton's quote "If I have seen further it is by standing on ye shoulders of Giants" from a letter to Robert Hooke correctly acknowledges, such a work can never be done alone without work of many others having been carried out before and the help of people around one. Conversely, I hope that this work is a little stone in the construction of science upon that many others will continue to build.

My special thanks goes to Prof. Dr. Hans-Martin Henning on the one hand in his role as professor for giving me the opportunity to carry out this work under his supervision on the other hand in his role as head of Fraunhofer ISE for his countless efforts to keep this institute up and running, making this and many other theses possible in the first place. My thanks goes also to Prof. Dr. Christoph Janiak who accepted to be the second examiner for the thesis.

I would also like to express my deepest gratitude to Dr. Stefan Henninger, he accompanied me along the path of this thesis. Thanks for putting the trust in me in to tackle this project in the beginning, thanks for giving me the time and freedom to work on this thesis, thanks for all the advice, support, tips and positive attitude and thanks for the content-related supervision of this thesis and the proof-reading.

I would like to thank my actual and former colleagues from the Fraunhofer ISE material group that became friends along the way for the helping hands and open doors in scientific as well as in personal matters. You were the people that shared my successes and setbacks on a daily basis.

Thanks to the ISE group components for excellent collaboration and patient explanations; and thanks to whole Fraunhofer ISE institute with its countless possibilities of analytical methods and devices for the unbureaucratic help and assistance and also for the ISE spirit that makes it a pleasure to work in such a surrounding. Also, I would like to thank the partners from other institutes and the industry for the good collaboration. A big thanks goes to my friends and family whose support and believe in me keep me going every single day. From the bottom of my heart I would like to thank JoJo for everything – thank you.

0