Development and testing of nano-porous micro-carriers for corrosion inhibitor release from protective organic coatings

P.J. Denissen
Development and testing of nano-porous micro-carriers for corrosion inhibitor release from protective organic coatings

by

P. J. Denissen

to obtain the degree of Master of Science in Material Science and Engineering at the Delft University of Technology, to be defended publicly on Wednesday December 9, 2015 at 10:30 AM.

Student number: 1552058  
Project duration: January 5, 2015 – December 9, 2015  
Faculty: Aerospace Engineering  
Department: Aerospace Structures and Materials  
Group: Novel Aerospace Materials (NovAM)  
Thesis committee: Prof. dr. ir. S. van der Zwaag, TU Delft, NovAM, Chairman of thesis committee  
Dr. S. J. Garcia Espallargas, TU Delft, NovAM, Thesis supervisor  
Dr. Y. Gonzalez, TU Delft, MSE, External member

This thesis is confidential and cannot be made public until December 9, 2016.

An electronic version of this thesis is available at http://repository.tudelft.nl/.
“We are built to conquer environment, solve problems, achieve goals, and we find no real satisfaction or happiness in life without obstacles to conquer and goals to achieve.”

Maxwell Maltz
I would like to express my very great appreciation to my supervisor Dr. Santiago Garcia Espallargas for all his time, support, guidance and useful critique during my master thesis project at the NoVAM group. The weekly meetings and many (e-mail) conversations helped me to get familiar with new techniques and made it possible to get to most out of myself. In addition, he gave me the responsibility to choose my own path and take up the challenges in my own way. Special thanks to Prof. Sybrand van der Zwaag for his interest and vivid way of interpreting my work. I would also like to thank Frans Oostrum for his help in the physical lab with the scanning electron microscope and all the other equipment, but also for the times that we brainstormed about new solutions to the challenges I encountered. Many thanks to Johan Bijleveld and Lijing Xue to get familiar with working in a chemical lab and their help to set up new experiments. Also many thanks to Ruud Hendrikx for the technical support and measurements. Many thanks to all the NoVAM colleagues whom I have worked with for their help but more importantly for the great time I had. Their enthusiasm and the essential breaks for coffee or stronger alternatives certainly helped me in those moments of tediousness. Finally, I wish to thank my family and my girlfriend Ellen Klijnstra for their support and encouragement throughout my master, I could not have done it without them.

Paul Denissen
Delft, November 18th 2015
Abstract

The use of carriers doped with environmentally friendly corrosion inhibitors has been proposed in the last years as an alternative to existing highly efficient but toxic corrosion inhibitors based on chromium VI. Despite the promising results using synthetically produced nano-carriers, limitations related to their production and protection of big damages makes the search for carrier alternatives a necessary step for a successful introduction of the concept in industrial applications. This work explores for the first time the feasibility of using a biobased nano-porous silica micro-carrier obtained from the exoskeletons (frustules) of the algae group known as diatoms.

For the doping, frustules obtained from diatomaceous earth (fossil frustules) of one location where the main diatom species is *Aulacoseira* and Ce(NO$_3$)$_3$ as corrosion inhibitor were used. In order to evaluate the doping degree and release kinetics of the diatom frustules a new in-situ detection system was developed and validated. Out of this detailed study, one diatom-doped system was selected for further proof of the active corrosion protection in a coating system. For the purpose an epoxy coating and an aerospace aluminium alloy AA2024-T3 were used. The protection degree was then evaluated by an in-situ opto-electrochemical technique, combining crucial optical information about delamination and underfilm corrosion processes with electrochemical signals. In order to advice on the best possible carrier geometry for active corrosion protection and establish the first steps to the theoretical limits of the concept, a modeling approach was followed.

The work presented here demonstrates that the use of diatom frustules as carriers for active corrosion inhibition in coatings is feasible and very promising. The results show that, without further optimization of the formulation or the doping and release mechanism, protection of AA2024 coated plates of up to 27 days immersion in 0.05 M NaCl are possible. Moreover, two in-situ evaluation set-ups have been proposed and validated allowing future research in a much more efficient and reliable manner. Furthermore, the model applied in this work shows that the corrosion protection can be tuned by the carrier size and further optimized by using shapes with a high aspect ratio, combined with the implementation of controlled release systems and more efficient inhibiting agents. This work sets up the basis for future research in the use of the big diatom family with more than 10.000 different architectures as carriers for controlled release in coatings.
# Contents

List of Figures vii

List of Tables ix

Abbreviations x

1 Introduction 1
   1.1 Context of the project .............................................. 1
   1.2 Diatoms and their use in technology ............................ 3
   1.3 Scope of the thesis ............................................... 5
      1.3.1 From nano-particles to diatom frustules as corrosion inhibitor carrier .......................... 5
      1.3.2 Controlled release of corrosion inhibitors .................................. 6
      1.3.3 Research questions of the thesis ..................................... 7
   1.4 Outline of the thesis ............................................... 8

2 Doping of diatoms frustules 9
   2.1 Materials and characterization .................................... 9
      2.1.1 Materials ...................................................... 9
      2.1.2 Characterization .............................................. 9
   2.2 Obtaining intact frustules from Diatomaceous Earth ............... 10
      2.2.1 Water separation process ..................................... 10
      2.2.2 Chemical treatment .......................................... 13
   2.3 Corrosion inhibitor loading ........................................ 15
      2.3.1 Effect of loading methods ..................................... 15
      2.3.2 Effect of corrosion inhibitor types ............................ 18
   2.4 Conclusion ...................................................... 20
   2.5 Recommendations .................................................. 20

3 Inhibitor release from carrier systems 21
   3.1 Novel In-situ Release Kinetics Setup (InReK) ..................... 21
      3.1.1 Technique .................................................... 21
      3.1.2 Validation .................................................. 24
   3.2 Release kinetics from Ce(NO$_3$)$_3$ doped diatom frustules ....... 32
   3.3 Conclusion ...................................................... 33
   3.4 Recommendations .................................................. 33
## Contents

4 Corrosion protection of coatings containing inhibitor doped diatom frustules 34
4.1 Materials and methods ................................. 35
4.1.1 Materials ........................................ 35
4.1.2 Sample preparation ................................. 35
4.1.3 Characterization ................................... 37
4.2 Results and Discussion ............................... 39
4.2.1 Challenges during the coating production .......... 39
4.2.2 Passive corrosion protection ......................... 41
4.2.3 Active corrosion protection ......................... 42
4.3 Conclusion ........................................... 47
4.4 Recommendations .................................... 47

5 Effect of carrier geometry & size on the corrosion inhibitor release: a modeling approach 48
5.1 Particle packing algorithms .......................... 48
5.1.1 V1.0: Packing of spheres through static triangulation techniques .......... 49
5.1.2 V2.0: Packing of polyhedra through event-driven molecular dynamics and Monte Carlo displacement techniques .......................... 50
5.2 Modeling particle-containing coatings ................. 51
5.2.1 Boundary conditions ............................... 51
5.2.2 Particle geometries ................................ 51
5.2.3 Particle sizes .................................... 53
5.3 Model analysis ....................................... 54
5.3.1 Data-handling for particle packing models ........ 54
5.3.2 Mathematical representation for a damaged coating in corrosive environment .......................... 56
5.4 Results and discussion ............................... 58
5.4.1 Effect of carrier shape on the corrosion inhibitor release concentration .......... 58
5.4.2 Effect of carrier size on the corrosion inhibitor release concentration ........ 62
5.5 Conclusion ........................................... 65
5.6 Recommendations .................................... 65

Conclusion 67

A Technical datasheet - DiaFil 525 68

B Particle Size Distribution Diagram for Diafil 525 69

C SEM-EDX results for diatom frustules loaded methods with Ce(NO₃)₃ 70
C.1 Loading by dispersion at 23 °C .......................... 70
C.2 Loading by dispersion at 60 °C ......................... 71
C.3 Loading by capillarity ................................ 72
C.4 Loading in saturation ................................ 73

D XRD analysis 74
D.1 As received Diafil 525 ................................. 75
D.2 Water separated diatom frustules loaded with Ce(NO₃)₃ by loading in saturation .......... 76
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Representation of diatoms</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Different types of release kinetics</td>
<td>6</td>
</tr>
<tr>
<td>2.1</td>
<td>SEM image of the as received Diatomaceous Earth (DE) DiaFil 525</td>
<td>10</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic representation of a diatom frustule</td>
<td>11</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic representation of the water separation setup</td>
<td>12</td>
</tr>
<tr>
<td>2.4</td>
<td>SEM images of the as received (a), and water separated DE, (b) the water separation process, as well as the EDX analysis (c)</td>
<td>12</td>
</tr>
<tr>
<td>2.5</td>
<td>SEM-EDX spectra of the DE treated by the 3 different chemical treatments compared to the water separated DE</td>
<td>14</td>
</tr>
<tr>
<td>2.6</td>
<td>Schematic representation for the loading methods</td>
<td>15</td>
</tr>
<tr>
<td>2.7</td>
<td>SEM-EDX spectra for unloaded and loaded diatom frustules with Ce(NO$_3$)$_3$ using different loading methods.</td>
<td>16</td>
</tr>
<tr>
<td>2.8</td>
<td>SEM images loaded diatoms</td>
<td>17</td>
</tr>
<tr>
<td>2.9</td>
<td>Doping diatom frustules with different corrosion inhibitors</td>
<td>18</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematics of the In-situ Release Kinetics Setup (InReK)</td>
<td>21</td>
</tr>
<tr>
<td>3.2</td>
<td>Illustration of the InReK stirring device</td>
<td>23</td>
</tr>
<tr>
<td>3.3</td>
<td>InReK cuvette containing semipermeable membrane</td>
<td>24</td>
</tr>
<tr>
<td>3.4</td>
<td>InReK validation results</td>
<td>25</td>
</tr>
<tr>
<td>3.5</td>
<td>InReK threelfold reproducibility test</td>
<td>26</td>
</tr>
<tr>
<td>3.6</td>
<td>Effect of changing of stirring speed</td>
<td>27</td>
</tr>
<tr>
<td>3.7</td>
<td>Graphical illustration of the effect of stirring speed on the water-flow inside the cuvette</td>
<td>28</td>
</tr>
<tr>
<td>3.8</td>
<td>Effect of changing the amount of Ce(NO$_3$)$_3$ inside the filter to 2.0, 3.5 and 5.5 mg</td>
<td>28</td>
</tr>
<tr>
<td>3.9</td>
<td>Graphical illustration of the amount of corrosion inhibitor inside the filter located on top of the cuvette</td>
<td>29</td>
</tr>
<tr>
<td>3.10</td>
<td>Effect of changing the filter type</td>
<td>30</td>
</tr>
<tr>
<td>3.11</td>
<td>Cross-sectional illustration of three different types of paper filter</td>
<td>30</td>
</tr>
<tr>
<td>3.12</td>
<td>The effect of changing (a) diatom frustule cleaning treatments and (b) amount of Ce(NO$_3$)$_3$ per diatom frustule on the release kinetics</td>
<td>32</td>
</tr>
<tr>
<td>4.1</td>
<td>Illustration of the corrosion protection mechanism of coatings containing inhibitor-doped diatom frustules</td>
<td>34</td>
</tr>
<tr>
<td>4.2</td>
<td>Schematic representation of the in table 4.1 presented coatings</td>
<td>36</td>
</tr>
<tr>
<td>4.3</td>
<td>Illustration of the three electrode Opto-Electrochemical cell setup</td>
<td>37</td>
</tr>
<tr>
<td>4.4</td>
<td>Coating after curing for (a) unloaded and (b) Ce(NO$_3$)$_3$ loaded diatom frustules</td>
<td>39</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>SEM image (a) of the coating containing Ce(NO$_3$)$_3$ loaded diatoms, (c) at higher magnification including an elemental line-mapping, together with the 2D elemental mappings (b) and (d) for Si, Ce and C.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EIS results via (a) impedance modules and (b) phase plots for intact epoxy coatings after 5h and 72h immersion in 0.05M NaCl.</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>Bode and phase plots at the turning points of the low frequency bode modules evolution.</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>Acquired OCP during (a) the first 72 hours up to (b) 30 days and (c) the total impedance bode modules acquired at 0.01Hz up to 30 days.</td>
<td></td>
</tr>
<tr>
<td>4.9</td>
<td>Scratched coatings during immersion in 0.05M NaCl inside the opt-electrochemical setup.</td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>Flowchart of the parking algorithm.</td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>Platonic solids.</td>
<td></td>
</tr>
<tr>
<td>5.3</td>
<td>Archimedean solids.</td>
<td></td>
</tr>
<tr>
<td>5.4</td>
<td>Cylindrical shapes with different aspect ratios.</td>
<td></td>
</tr>
<tr>
<td>5.5</td>
<td>Cuboids.</td>
<td></td>
</tr>
<tr>
<td>5.6</td>
<td>Simulation process that is used gain the particle data.</td>
<td></td>
</tr>
<tr>
<td>5.7</td>
<td>Graphical representation of a coating that is damaged, followed by filling the damage with electrolyte.</td>
<td></td>
</tr>
<tr>
<td>5.8</td>
<td>The effect of using uni-dimensional platonic, archimedean and spherical solids on the concentration of released corrosion inhibitor of scratches of different widths.</td>
<td></td>
</tr>
<tr>
<td>5.9</td>
<td>Realistic electrolyte exposures at the scratch.</td>
<td></td>
</tr>
<tr>
<td>5.10</td>
<td>Illustration of the circumradius.</td>
<td></td>
</tr>
<tr>
<td>5.11</td>
<td>Effect of using multi-dimensional solids on the concentration of released corrosion inhibitor of scratches of different widths.</td>
<td></td>
</tr>
<tr>
<td>5.12</td>
<td>Effect of using different cuboid shapes with aspect ratios on the release at the damaged site width.</td>
<td></td>
</tr>
<tr>
<td>5.13</td>
<td>The simulated effect of changing the size of spherical particles in the coating on the concentration of released corrosion inhibitor of scratches of different widths.</td>
<td></td>
</tr>
<tr>
<td>5.14</td>
<td>The effect of changing the wall boundary conditions from periodic to for solid for the results shown in figure 5.13.</td>
<td></td>
</tr>
<tr>
<td>5.15</td>
<td>Effect of particle size and release type on the corrosion protection.</td>
<td></td>
</tr>
</tbody>
</table>
# List of Tables

3.1 Properties for cellulose paper filters .............................................. 29
4.1 Compositions for the coated substrates ............................................ 36
4.2 Scratch properties for the coatings used for the corrosion protection analysis ............................................ 37
5.1 Different particle sizes used in the different models ......................... 62
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>2 Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>3 Dimensional</td>
</tr>
<tr>
<td>Ce(NO₃)₃</td>
<td>Cerium Nitrate Hexahydrate</td>
</tr>
<tr>
<td>DDS</td>
<td>Drug Delivery System</td>
</tr>
<tr>
<td>DE</td>
<td>Diatomaceous Earth</td>
</tr>
<tr>
<td>EDMD</td>
<td>Event Driven Molecular Dynamics</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-rays</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>IMC</td>
<td>Intermetallic Compound</td>
</tr>
<tr>
<td>InReK</td>
<td>In-situ Release Kinetics</td>
</tr>
<tr>
<td>IRR</td>
<td>Infrared Reflectography</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>LiCl</td>
<td>Lithium Chloride</td>
</tr>
<tr>
<td>LS</td>
<td>Lubachevsky-Stillinger</td>
</tr>
<tr>
<td>MATLAB</td>
<td>MATrix LABoratory</td>
</tr>
<tr>
<td>MCM</td>
<td>Mobil Composition of Matter</td>
</tr>
<tr>
<td>Na-2-MBT</td>
<td>Natrium-2-Mercaptobenzothiazole</td>
</tr>
<tr>
<td>Na-DEDTC</td>
<td>Natrium-diethylthiocarbamate</td>
</tr>
<tr>
<td>NovAM</td>
<td>Novel Aerospace Materials</td>
</tr>
<tr>
<td>OCP</td>
<td>Open Circuit Potential</td>
</tr>
<tr>
<td>OES</td>
<td>Optical Emission Spectrometry</td>
</tr>
<tr>
<td>OpenGL</td>
<td>Open Graphics Library</td>
</tr>
<tr>
<td>PVC</td>
<td>Pigment Volume Concentration</td>
</tr>
<tr>
<td>RGB</td>
<td>Red Green Blue</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions Per Minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SVET</td>
<td>Scanning Vibrating Electrode Technique</td>
</tr>
<tr>
<td>USB</td>
<td>Universele Serial Bus</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-Violet</td>
</tr>
<tr>
<td>VIS</td>
<td>Visible</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

This introduction chapter is meant to provide the reader with the means to understand the work that is presented in this thesis. In section 1.1 the reasons behind the initiation of the project are explained. In section 1.2 a brief introduction on diatoms and their use in technology is presented in order to give the reader the required knowledge on the material in question. The scope of the thesis is presented in section 1.3 by placing the context into perspective through the gained knowledge on diatoms. The last section, 1.4, explains the outline of this thesis.

1.1 Context of the project

This project was proposed by the supervisor Dr. S. J. Garcia Espallargas, assistant professor in the Novel Aerospace Materials Group (NovAM) at the Delft University of Technology where he works in the field of self-healing polymeric materials, corrosion protection and coatings technology.

This project comes forth from the importance of developing new environmentally friendly coating systems that combine passive (e.g. barrier) and active (e.g. corrosion inhibitors) corrosion protection through self-healing mechanisms. Corrosion is the result of (electro)chemical reactions between a metal or metal alloys and its environment (e.g. sodium chloride solutions) [1, p. 1-10]. Aluminum alloy AA2024-T3 containing 5% Cu is often used in aerospace structures because of its increased strength by intermetallic compound phases (IMC) [2, p.223-254]. However, these IMC phases also reduce its corrosion resistance due to the formation of complex galvanic couples. Some of these IMC phases are cathodic to the matrix, (e.g. Al₂Cu and Al₂₀Cu₂(FeMn)₃), whereas others are anodic (e.g. Al₂CuMg) [3–7].

The use of coatings is one of the most cost-effective and widespread approach for passive corrosion protection of metallic substrates [8]. The coating provides a physical barrier to the underlying substrate, preventing the ingress of corrosive fluids at the metallic surface [9]. However, coatings remain vulnerable to damages whereby they loose their barrier protective capacities. Active corrosion protection systems such as corrosion inhibitors are introduced into the coating to prevent further loss of the coating protective function. For decades, toxic and carcinogenic Cr⁶⁺-based particles were used as the most widespread corrosion inhibitors [10]. However, the Authorization and Restriction of Chemicals (REACH) has banned the consumption of chromates in many applications [11], which means that alternatives have to be looked for. Cerium salts proved to be one of the most promising chromate replacement inhibitors. The Ce³⁺ cation is believed to suppress corrosion of AA2024-T3 by gradual formation of an insoluble hydroxide or oxide layer on the IMC phases [12, 13]. Also other replacement inhibitors have been used such as lithium salts [14, 15], lantanides [16] and organic mercaptobenzothiazoles [17] and diethyldithiocarbamates [18].

However, the implementation of these new corrosion inhibitors resulted in unwanted reactions with the
surrounding coating matrix [19]. These inhibitor-matrix interactions can be reduced by encapsulating the corrosion inhibitors inside carriers. Furthermore, the release of the corrosion inhibitors from these carriers becomes controllable. The use of triggers such as changes in pH [20] and ion-exchange [21, 22] have shown to be successful methods for controlled release and are described as self-healing mechanisms. Additionally, several different carriers have been used such as bentonites [23], hydrotalcites [24], halloysites [25], and zeolites [21, 22]. Despite the successful results of the carrier systems, efficient and long-term corrosion protection for large damages (>100 µm) has not yet been realized. This is probably due to the insufficient release kinetics and/or amount of corrosion inhibitor at the damaged location. The understanding of the limitations of current carriers and the need for better and environmentally friendly alternatives is the foundation of the work that will be presented in this thesis.

In this project, the tasks given to the student was to investigate the development en testing of 3D porous inorganic exoskeletons of natural underwater diatoms as bio-based silica micro-carriers for the active corrosion protection by release of corrosion inhibitors from self-healing protective coatings. Before the start of the project, neither supervisor nor student had worked with diatoms before. To the best knowledge of the research team involved in this MSc. thesis, no applications for controlled release of corrosion inhibitors from diatoms had been explored elsewhere. Because of this, a foregoing literature study was performed in order to broaden the expertise on the potential use for diatoms as carrier system in general, combined with the development of innovative experimental techniques required for this investigation. Moreover, the work presented by the student is meant as a feasibility study, whereas the actual creation of a perfectly working corrosion inhibiting system does not belong to the primary goals for this work.

The project was supported by the company Profiltra Customized Solutions who provided diatomite materials. The research facilities and experience within the NovAM group were made available to the student. The foregoing literature research on behalf of the student commenced on November 18th 2014. The actual graduation work presented in this thesis started on January 5th 2015 and finds its conclusion on December 9th 2015 after which roughly 10 months FTE were spend on project work. The final outcome of the graduation thesis will be assessed by an exam committee composed of the chairman Prof. dr. ir. S. van der Zwaag (Head of the NovAM group), supervisor Dr. S. J. Garcia Espallargas and Dr. Y. Gonzalez as external member.
Chapter 1. Introduction

1.2 Diatoms and their use in technology

Diatoms are symmetrical unicellular micro-organisms ranging in size from 2 \( \mu m \) up to 2 \( mm \) and often exist in colonies in the shape of filaments or ribbons. The name diatom originates from the Greek word *diatomos* meaning cut in two, revering to their bilateral symmetry [26]. Diatoms are a major group of eukaryotic algae (containing a nucleus and other organelles enclosed within membranes). Diatoms collect energy from the sun through photosynthesis, it is estimated that the photosynthetic activity of diatoms produces between 20 and 40% of the earth's oxygen.

There are +200 genera of living diatoms, and it is estimated that there are approximately \( 10^5 - 10^6 \) extant species, whereas new and diverse forms are still being discovered. Diatoms can be found in nearly every water habitat (e.g. oceans, freshwater, soils, and on damp surfaces).

Even though the existence of diatoms dates back to the Jurassic age [27], their study started relatively late in comparison with other groups of micro-organisms. Diatoms were first observed in 1703 by the Dutch scientist Antoni van Leeuwenhoek from Delft through his handcrafted microscope [28, p.1-6]. In the last century, the availability of the commercial Scanning Electron Microscopes (SEM) and other computational tools made it possible to extend the study on diatoms to a higher level. The precision of measurements enabled Round et al. (1990) to describe the complete treatment of diatom morphology and ecology [28, p.1-6].

Figure 1.1 shows (a) diatom colonies, (b) the exoskeleton of two types of diatoms including a schematic illustration of the porous valve structure, and (c) the fossilized remaining Diatomaceous Earth.

The hallmark for the diatom is its exoskeleton made of hydrated silicon dioxide. The exoskeleton is called frustule and consists of two large valves linked together with structures termed girdle bands. The shape can best be compared to pill-box. The frustule (in fossilized form) is shown in figure 1.1(c) and is referred as Diatomaceous Earth (DE) or diatomite [28, p.1-6] and can be found on sea and riverbeds. Due to this, millions of tonnes of DE are available as waist-product in the mining industry [29]. Diatoms are traditionally classified into two orders of frustule symmetry (centric and pennate) as can...
be seen in figure 1.1(b). The first category is *Centric* diatoms, which are radially symmetrical and thereby almost approach isodiamicetricity. The second category is *pennate* diatoms, which have bilateral symmetry. [28, p.17-23]

The frustule valves are build up out of ribs which grow out from a circular (*centric* diatoms) or elongate (*pennate* diatoms) patterned center. These ribs are cross-linked by short lateral ribs to form a porous primary network called the *Areola*. Superposition of more silica during the valve deposition can further complicate the valve with secondary *Cribrum* and tertiary *Cribellum* networks. In the schematic illustration of figure 1.1(b) it can be seen that the pore size of the *Areola* network varies between 500nm and 1 µm in diameter, whereas the smallest pore size in the *Cribrellum* network can reach 40 nm in diameter, depending on the species. [28, p.29-34][30, 31]

The highly porous pill-box structure of these silica frustules makes them very interesting for a very broad variety of fields and applications in technology. Filtration [32–34] is the most well-known application for DE, whereby the frustule pores separate unwanted solid particles from from the fluid. The frustules are also used as replicators [35–37] and templates [38–41] for the development of micro- and nano-fabricators, making it possible to use frustule-like structures that are not yet producible through conventional methods. The photosynthetic nature of diatoms makes them also interesting for biophotonics, whereby they can be used as photonic wave-guides [42], collectors [43–45] and biosensors [46–49]. In the near future, functionalized diatoms could even be applicable as sensors on lab-on-a-chip platforms [50].

Recently, the field of medicine became interested in using the diatom frustules for Drug Delivery Systems (DDS). The drug molecules can be doped inside the frustules to enhance the kinetics and eliminate premature release. Furthermore, DDS systems have to be non-toxic, non-immunogenetic, biodegradable, easily (re)producible, and most important of all, cheap. The group of Losic [29, 51–56] and recently also by others [57–61] showed that diatom frustules meet these requirements and can be used as promising DDS. To the best knowledge of the research team involved in this MSc. thesis, there have been no applications of diatoms for controlled release in engineering applications such as coatings representing this thesis the very first attempt to use them in coatings for controlled release of corrosion inhibitors.
Chapter 1. Introduction

1.3 Scope of the thesis

The scope of this thesis is to develop and test the use of diatom frustules as bio-based silica micro-carriers for corrosion inhibitor release in protective coatings. Ergo, it is crucial that frustules can actually store and release corrosion inhibitors. Furthermore, active corrosion protection from damaged coatings containing inhibitor-doped frustules has to be confirmed. Additionally, the advantages of diatom frustules by their architecture and biodiversity has to be investigated. The reasons for using diatom frustules as corrosion inhibitor carrier and the importance of inhibitor release kinetics are explained respectively. This information is then used to formulate the research questions presented in section 1.3.3.

1.3.1 From nano-particles to diatom frustules as corrosion inhibitor carrier

Inorganic 2D lamellar nano-particles (e.g. montmorillonites [62], bentonites [23] and hydrotalcites [24]) and 3D nano-particles (e.g zeolites [21, 22] and halloysites [25]) have been used as carriers for corrosion inhibitors. These particles showed potential but their use remains limited by their versatility and limited release capacity. This resulted in insufficient release to protect large damages (>100 \( \mu m \)) for a longer period of time.

From the above mentioned limitations it became clear that larger carriers (microparticles instead of nano-particles) are required to increase the volume capacity of corrosion inhibitors inside the carriers. Synthetic silica-based mesoporous microstructures (e.g. MCM-41 and SBA-15) currently used for therapeutic drug delivery [63, 64] are proposed as corrosion inhibitor carrier because these particles are tunable in morphology and size. However, the current production technologies are still rather limited and time-consuming, making them too expensive to be used in the large quantities required for coating systems. This is where biological grown silica micro-particles (i.e. diatom frustules) become interesting as carrier, because they are not dependent on production possibilities and the involved costs. Moreover, the use of the diatom frustules is supported by several key facts:

- **Architecture:** Pill-box structure combined with the large size range from 2 \( \mu m \) up to 2 mm and porous walls with diameters ranging between 40 nm and 1 \( \mu m \).
- **Biodiversity:** Approximately \( 10^5 \) – \( 10^6 \) species with all their own complex shape and size.
- **Availability:** Relatively easily cultivated and their fossilized diatom frustules (DE) can be found in large quantities in soils.

The above mentioned advantages make it possible to select the ideal frustule type for long-term release of corrosion inhibitors for superior protective coatings. However, the question remains which size and shape results in the best performance. To the best knowledge of the research team involved in this MSc. thesis, the effect of changing the size and shape of corrosion inhibitor carriers has not yet been studied. The current limitations of nano-particles have been shown but it has never been proven that larger or differently shaped carriers result in better performance. Experimental research to find the ideal shape and size is also rather complicated. Many different coatings with different carriers of known size and shape have to be produced and tested. A more feasible solution at this stage would be to model the effect of carrier size and shape on the release of corrosion inhibitor from a damaged coating. Therefore a modeling approach will be used in this thesis to investigate the effect of the size and geometry of the carrier system on the corrosion inhibitor release.

Modeling has been used for a similar concept by Mookhoek et al. [65] to show that elongated capsules have a positive influence on the release of liquid healing agent per crack area through a numerical study. Furthermore, mathematical-analytical models [66–68] have been used to determine the release kinetics of different corrosion inhibitors from damaged coatings. Nowadays, modeling the size and shape of particles inside a coating can be achieved through particle packing methods. The development of better and faster particle packing programs have increased significantly the last decade [69] due to the...
increase of computational power and more advanced algorithms. They have been used for many known structures, e.g. rocket propellants [70], chain polymers [71], fiber-reinforced materials [72], cement & concrete materials [73], and could in our case be used for the packing of particles inside corrosion protective coatings. This would allow us to predict the ideal size and shape for the carriers without actually making the coatings.

1.3.2 Controlled release of corrosion inhibitors

While diatoms seem to be the ideal candidate as carrier for corrosion inhibitors, the specific type of release that is required for long-term corrosion protection still needs to be achieved. Javierre et al. [66] shows that fast and short initial release of inhibitors is needed to produce a fast corrosion protection while keeping sufficient stored inhibitor for future release events. This should be followed by a slow release over a long period of time or triggered fast release when needed to maintain the supply of corrosion inhibitors. Additionally, there is a certain concentration required ($C_{\text{min}}$) before active protection occurs and a level ($C_{\text{max}}$) when the protection decreases again [16]. Figure 1.2 shows different types of release kinetics.

![Figure 1.2: Different types of release kinetics, a) unwanted release kinetics with slow initial or instant release (dashed line), b) Multi-kinetic release, and c) on-demand release. $C_{\text{min}}$ and $C_{\text{max}}$ show the minimum and maximum required released amount for the system.](image)

In figure 1.2 it can be seen that we speak of ”unwanted release” (a) when all the corrosion inhibitor is released instantly (dashed line) or when the initial release takes too long (solid lines), ”multi-kinetic release” (b) when a fast initial release is followed by a longer slow release, and ”on demand release” (c) when the corrosion inhibitor is only released when required.

The control of release kinetics is of great importance for active corrosion protection [20, 22, 74, 75], but also in other fields such as medicine [29], polymers [76], concrete [77], asphalt [77], and fiber composites [78]. Ferrer et al. [22] has already shown that controlled multi-kinetic release of corrosion inhibitor can be obtained through the use of double doped zeolites (3D nano-carriers), whereby a short initial release is followed by a longer on-demand release triggered by ion-exchange. Chen and Fu [20] have also shown that on-demand release is possible through the use of pH triggered nano-valves applied on messoporous silica.

For diatom frustules, Losic et al. [51] has proposed multi-kinetic release from doped diatom frustule carrier systems for drug delivery. The morphology of the frustules combined with surface treatments resulted in a fast initial release from the (outer) surface combined with a longer slow release from the internal pores, both through desorption mechanisms. This illustrates the potential of using diatom frustules for multi-kinetic and even on-demand release of corrosion inhibitors when certain particle
modifications or treatments are applied.

Measuring the actual release kinetics from carrier systems is an important step before carrier modification for multi-kinetic or on-demand release can be explored. The traditional technique to measure the release kinetics is simply done by sampling the doped carrier systems dispersed in solution at specific time-intervals. The concentration of the dopant is measured through experimental methods such as light spectroscopy or Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) [22, 52, 74]. Despite the simplicity of the method, there are some major flaws that can cause incomplete and even incorrect results. One major flaw is that fast occurring kinetics is often overseen because the sampling time is too long, resulting in insufficient datapoints. Furthermore, measurements taken from mixtures that are stirred to increase dispersion are not realistic where the doped system should remain stationary. Because of these reasons it became clear that a better procedure is required to accurately measure the release kinetics for corrosion inhibitor doped carrier systems before any conclusions can be made on their effect. For this reason a new setup to measure the release kinetics of corrosion inhibitors from carrier systems will be discussed in this thesis.

1.3.3 Research questions of the thesis

The scope of the thesis resulted into the following four research questions:

- Is it possible to dope diatom frustules with corrosion inhibitors?
- Can we measure the release kinetics of corrosion inhibitors from carrier systems in-situ?
- Can we show that corrosion inhibitor doped diatom frustules can be used for active corrosion protection in coatings?
- What is the effect of the size and geometry of the carrier systems on the corrosion inhibitor release?

This work can be seen as a proof of concept and as starting point for further development in the use of diatom frustules as carriers of functional species for engineering applications such as protective coatings.
1.4 Outline of the thesis

In this thesis the development and testing of diatom frustules for corrosion inhibitor release in protective coatings is discussed. This is done by answering the research questions described in section 1.3.3. Each of the following chapters is used to answer a separate research question.

Chapter 2 describes the doping of diatom frustules with organic and inorganic corrosion inhibitors. First the diatom frustules are obtained from diatomaceous earth. These diatom frustules are used in several treatments to load them with organic and inorganic corrosion inhibitors.

Chapter 3 describes a new method to measure the release kinetics of corrosion inhibitors from carrier systems. The development of the method is discussed and followed with an extensive validation procedure. The method is finally used to show that inhibitor release from carrier systems can be measured by using corrosion inhibitor doped diatom frustule prepared as discussed in chapter 2.

Chapter 4 describes several coatings that contain corrosion inhibitor doped diatoms as proof of concept that they can be used for active corrosion protection. The preparation steps and challenges during the production process are presented. The active and passive corrosion protection of these coatings are tested through the use of electrochemical impedance spectroscopy combined with in-situ optical inspection of the damaged coating.

Chapter 5 describes the effect of changing the size and geometry of the carrier systems on the corrosion inhibitor release. This is done through a modeling approach whereby a particle packing method is used to model carrier containing coatings. The boundary conditions and methods are described and a mathematical representation for a damaged coating in corrosive environment is given. The results of the model are used to study the influence of carrier geometry and size on the concentration of released corrosion inhibitor at scratches of different widths.

This thesis ends with a conclusion on the feasibility of diatom frustules for corrosion inhibitor release in protective coatings. Additional results and information can be found in the Appendix.
Chapter 2

Doping of diatoms frustules

Storing inhibitors inside the diatom frustules is the trivial and crucial step before the corrosion inhibitor release in self-healing protective coatings can be investigated. Therefore, the doping of diatom frustules with several organic and inorganic corrosion inhibitors is discussed in this chapter. In section 2.1 the used materials and characterization methods are introduced. This is followed with the obtention of intact diatom frustules from diatomaceous earth (DE) in section 2.2. This is done through a water separation method (2.2.1) and chemical treatments (2.2.2). In section 2.3 the doping of the obtained diatom frustules is presented. Several different loading methods (2.3.1) and corrosion inhibitor types (2.3.2) are discussed. The final conclusion on the work is given in section 2.4 and the chapter ends with the recommendations in section 2.5.

2.1 Materials and characterization

2.1.1 Materials

Diatomaceous Earth (DE) DiaFil 525 was supplied by Profiltra Customized Solutions. The particles have a mean particle size of 12 $\mu m$ and appear as fine white powder. The DE consist for 89.0 wt% out of silica ($SiO_2$). Appendix A contains the technical datasheet for DiaFil 525 for more information. Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and Sodium-diethyldithiocarbamate (Na-DEDTC), both with > 99% purity were purchased from Sigma-Aldrich. Lithium Chloride (LiCl) with > 99 % purity was purchased from Acros Organics and Sodium 2-Mercaptobenzothiazole (Na-2-MBT) with > 97 % purity was purchased from TCI. All aqueous solutions were prepared using Milipore® Elix 3 UV filtered water.

2.1.2 Characterization

To confirm the effect of the cleaning processes and to verify the presence, location and quantity of corrosion inhibitors after doping, field emission scanning electron microscopy, FESEM (JEOL JSM-840) coupled with Energy Dispersive X-rays (EDX) spectroscopy for elemental analysis was used. A small amount (less than a milligram) of DE was deposited on a black carbon conductive double adhesive tape, and coated with an ultrathin gold layer (15nm) before imaging.

Particle size evaluation was performed with Mastersizer 2000 (Malvern Inst. Ltd., UK), which uses a laser light scattering technique on dispersed particles.

X-ray diffraction (XRD) was employed to analyze the chemical composition of cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) after doping. For the measurements a Bruker D8 Advance diffractometer Bragg-Brentano geometry and Lynxeye position sensitive detector was used.
Chapter 2. *Doping of diatoms frustules*

2.2 Obtaining intact frustules from Diatomaceous Earth

Figure 2.1 shows the Scanning Electron Microscope (SEM) image of the as received diatom frustules used in this work.

![SEM image of the as received Diatomaceous Earth (DE) called DiaFil 525.](image)

As can be seen in figure 2.1, the as received frustules are mixed with high amounts of smaller particle size residue (e.g. clay, other oxides, and broken frustules) which are unwanted. Multiple cleaning steps will be conducted on the as received DE in order to obtain clean diatom frustules. The first step separates the intact diatom frustules through a water settling process. The second step purifies the intact frustules through chemical treatments using acid and alkaline solutions.

2.2.1 Water separation process

The separation step in this study is based on the work of Zhang et al. [79] where Stokes law is used to separate non-spherical diatom valves and gridle bands from *Coscinodiscus* diatomite. For our approach the technique is simplified and used only to separate the broken frustules from the intact ones. Stokes law states that the surface contact stress of the object is depended on the shape, resulting in different settling velocities for each shape [80]. The theory can be expressed with the following equation [79]:

\[
v = \frac{(\rho_s - \rho_0) g \cdot V}{k \mu \sqrt{S}}
\]

where,

- \(v\) is the settling velocity in \(m \cdot s^{-1}\)
- \(\rho_s\) is the specific gravity of the particles, which is 2.3 \(g \cdot cm^{-3}\) for DiaFil 525
- \(\rho_0\) is the density of the liquid medium, which is 1.0 \(g \cdot cm^{-3}\) for water at room temperature
- \(g\) is the acceleration of gravity of 9.81 \(m \cdot s^{-2}\)
- \(V\) the volume of intact particle in \(m^3\)
- \(k\) is the drag coefficient of 10.63 (valid for 10 – 100 \(\mu m\) sized particles)\(^1\)

\(^1\)No derivation or reference was given by Zhang et al. [79] for this value.
Chapter 2. *Doping of diatoms frustules*

\( \mu \) is the fluid viscosity, which is \( 0.8937 \cdot 10^{-3} \text{ Pa} \cdot \text{s} \) for water at room temperature. 

\( S \) is the particle cross-section area perpendicular to settling orientation in \( m^2 \), which will be discussed in more detail in the section below.

The equation shows that particles with a large volume and a small cross-sectional area settle faster compared to particles (of the same material) with a small volume and a large cross-sectional area. The volume and cross-sectional area for the diatom frustules are required to calculate the settling speed through equation 2.1. A model for the diatom frustules was derived in order to gain this information. Figure 2.2 shows the model for a diatom frustule.

![Figure 2.2: Schematic representation of a diatom frustule; (left) outer shape with inset showing the pore area fraction, (right) free space inside.](image)

From figure 2.1 it was found that the main species in the diatomite is the cylindrical diatom frustule from the species *Aulacoseira* [53]. It can be seen in figure 2.2 that the shape of a diatom frustule was therefore assumed to be a hollow cylinder with an outer radius \( R \), inner radius \( r \) and height \( h \). The wall of the frustule also consists out of small circular pores.

The volume of the diatom frustule \( V_{DE} \) can be defined by

\[
V_{DE} = \frac{2}{3} \pi (R^2 - r^2)h
\]  

(2.2)

which is simply the equation to calculate the volume of a hollow cylinder, where \( \frac{2}{3} \) represents the assumed \( \frac{1}{3} \) volume loss for the small pores, based on the pore area fraction as shown in figure 2.2.

The cross-section area can be calculated either as a circle with one large inner hole, or as a rectangle with small holes.

\[
S_{\text{Circle}} = \pi (R^2 - r^2)
\]  

(2.3)

\[
S_{\text{Rectangle}} = \frac{2}{3} Rh
\]  

(2.4)

The mean particle size of the diatomite is 12 \( \mu m \) based on the technical datasheet for DiaFil 525 (see Appendix A). However, figure 2.1 also shows that there is a large size distribution between the different diatom frustules. Ideally, the process should only remove broken particulates and all diatom sizes should be kept. Because of this, a smallest and a largest size diatom was assumed. The smallest diatom was estimated to have an outer radius \( R \) of 3 \( \mu m \), an inner radius \( r \) of 2.5 \( \mu m \) and a height of 3 \( \mu m \), which gives the slowest settling speed of \( 9.5 \cdot 10^{-6} \text{ m} \cdot \text{s}^{-1} \) through equation 2.1. The largest diatom was estimated to have a outer radius \( R \) of 10 \( \mu m \), an inner radius \( r \) of 9 \( \mu m \) and a height of 15 \( \mu m \), which will give the fastest settling speed of \( 1.0 \cdot 10^{-4} \text{ m} \cdot \text{s}^{-1} \) through equation 2.1. This means that the smallest...
Chapter 2. Doping of diatoms frustules

diatoms requires roughly 20 minutes to settle 1 cm, and the largest diatoms only 2 minutes.

The above calculations have been used as the first order approximation for the settling times. The experimental setup for the water separation method is shown in figure 2.3.

Figure 2.3: Schematic representation of the water separation setup where the big black dots are intact frustules and the small dots the broken particulates.

The best separation of intact frustules was achieved by using a 144mm diameter flat beaker, 8.0 grams of DE (sonicated for 30 minutes to loosen the broken particulates) and 120 ml of demineralized water, resulting in a height of 1 cm as can be seen in figure 2.3. This was left in unstirred condition for 30 minutes to allow the DE particles to settle down. The supernatant (containing the debris and broken frustules) was discarded with the use of a glass pipette. This settling process was repeated 5 times (without sonication), using 30 minutes as settling time. Finally the diatoms are filtered and water cleaned with the use of a Whatman® grade 595 paper filter and placed in a vacuum oven at 60°C for 24 hours, after which all the excess water was evaporated.

Figure 2.4 shows SEM images of the as received (a), and water separated (b) DE, as well as the EDX-analysis (c).

Figure 2.4: SEM images of the as received (a), and water separated (b) DE, as well as the EDX analysis (c).

From figure 2.4(a) it can be seen that untreated DE is a mixture of broken and intact diatom frustules. It contains many different sizes of mainly cylindrical frustules packed together. The outer surface of the
Chapter 2. Doping of diatoms frustules

frustules is contaminated with small particulates, probably broken frustules. On higher magnification (inset of figure 2.4(a)) it can be seen that the small particles clog up the pores of the frustules. After the water separation process the amount of broken frustules and other small micro-particles have been reduced significantly as can been seen in figure 2.4(b). This is confirmed by particle size measurements (see Appendix B) that show a higher volume fraction for particles with a mean particle size of 12 µm. On high magnification (inset of figure 2.4(b) it can be seen how the pores of the frustules are completely open as opposite to the as received ones.

The EDX spectrum\(^2\) (figure 2.4(c)) for as received (blue line) and water separated DE (red line) show that the largest constituents are silicon (Si) and oxygen (O), as expected for silica (SiO\(_2\)) frustules. Furthermore, small traces of Aluminium (Al), Iron (Fe), Calcium (Ca) and Magnesium (Mg) are present. Aw et al. [53] describe in their work that these elements can be related to impurity oxides (Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), CaCO\(_3\), CaO, and MgO). The EDX results after the water separation process shows the presence of the same elements in the same concentration as before the process, indicating that the treatment does not change the elementary composition of DE. It could be that the impurity elements are formed inside the frustule structure as oxides, or that they are small separate particulates which were not effectively removed by the process.

From this it can be concluded that the water separation process is very effective in extracting intact diatom frustules while maintaining a near mean particle size distribution. However, impurity elements remain present.

2.2.2 Chemical treatment

According to literature ([81]) the main impurities in the as received DE are clay, volcanic glass, organic matter and inorganic oxides such as Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), CaCO\(_3\), K\(_2\)O, Na\(_2\)O and MgO. These impurities limit the adsorption and desorption efficiency of DE because they can block the pores, thereby altering the surface area of the diatoms. In order to remove the impurities, chemical treatments with acid and alkaline solutions have been used to purify DE [82, 83]. In this work several chemical treatments (i.e. acid, alkaline and acid + alkaline) will be explored to purify the water separated diatom frustules.

For the acid treatment, 200 mg diatom frustules were dispersed in 20ml solution of 3.0 M Sulfuric acid (H\(_2\)SO\(_4\)) using a 50ml flask fitted with a condenser and controlled at 100°C in an oil bath. The flask was fitted with magnetic stirrer at around 200rpm. After 16 hours the content was filtered using a Whatman\(^\text{R}^\circledR\) grade 595 paper filter. The acid treated product was repeatedly washed with water until the filtrate reached a pH of 7. The residue was removed from the filter and dried in a vacuum oven at 60°C for 24 hours to completely dry.

For the alkaline treatment, 200 mg diatom frustules were mixed with 5.0 ml of sodium hydroxide solution (NaOH) having a pH of 11. The content was magnetically stirred for 1.5 hours at 200 rpm in a 50 ml flask. Finally the diatoms were filtered and water cleaned with the use of a Whatman\(^\text{R}^\circledR\) grade 595 paper filter until the filtrate reached a pH of 7. The residue was removed from the filter and dried in a vacuum oven at 60°C for 24 hours to completely dry.

The last treatment is a combination of the previous two with the acid followed by the alkali treatment.

Figure 2.5 shows the SEM-EDX spectra of the DE treated by the three different chemical treatments compared to the water separated DE.

\(^2\)The presence of Gold (Au) is due to a 15 nm gold layer that was deposited on the frustules in order to create a conductive surface. The elements Carbon (C), Zink (Zn) and Copper (Cu) are present due to the sample holder composition.
Chapter 2. Doping of diatoms frustules

Figure 2.5: SEM-EDX spectra of the DE treated by the 3 different chemical treatments compared to the water separated DE.

As can be seen in figure 2.5, all the treatments lead to the disappearance of elements related to contaminant oxides (Fe, Ca, Mg) leaving only the pure silica (SiO$_2$) diatom frustules available. Nevertheless, also a small peak related to Al remains. Yet, if the different chemical treatments are compared, it can be seen that the combined acid + alkaline treatment is the most effective in the removal of Al.

Apart from the elemental variations the treatments also produce changes in the particle size distribution, as can be seen in Appendix B. Only the acid treatment reduces the portion of small particles (< 10µ), this could be the removal of organic or inorganic impurities, but also the removal of small silica particles. A color change of the diatom frustules from light brown to white was also noticeable after the acid treatment, which is most probably due to the removal of organic matter. Visual inspection with the use of a SEM does not show changes in the morphology, structure or particle size distribution after the treatments. However, it could well be that the changes are not significant enough to detect through SEM.

It can be concluded that a purification process by settlement followed by chemical acid + alkaline pretreatments lead to pure diatom frustules with more open pores and with a narrower particle size distribution between 4 and 30 µm without large fractions of broken frustules.
2.3 Corrosion inhibitor loading

The effect of different loading methods and corrosion inhibitor types is treated respectively in this section of the thesis.

2.3.1 Effect of loading methods

Three different loading methods have been examined to prepare cerium doped diatom frustules. Figure 2.6 shows a schematic representation for these methods; (a) loading by dispersion, (b) loading in saturation, and (c) loading by capillarity.

![Figure 2.6: Schematic representation for the loading methods; (a) loading by dispersion, (b) loading in saturation, and (c) loading by capillarity action.](image)

The loading by dispersion is the process used to promote possible adhesion of cerium molecules dispersed in solution onto the surface of frustules. This adsorption is possible if there are active chemical attractions present (e.g. van der Waals forces or electrostatic potentials). This is the first explored method because it is considered to be a reliable, simple, efficient and cost-effective method [84]. Moreover, others [85–87] have shown that diatom frustules are effective adsorbents for heavy metals such as Lead(II) [85] and trivalent chromium [86, 87]. The technique was carried out by mixing 150 mg diatom frustules in 10 ml of 0.5 M $\text{Ce(NO}_3\text{)}_3$ and was executed at two different temperatures. The first mixture was kept at ambient temperature of 23°C in unstirred condition for 1.5 hours inside a 50 ml flask fitted with a condenser. The second mixture was controlled at 60°C in an oil bath with stirring at 200 rpm for 1 hour. Higher temperatures increases the movement of ions and promote possible ion-exchange. This principle is based on loosely held cations on the surface of the diatom frustules that are capable to be ion-exchanged with the soluble cerium cations. The contents of the mixtures was vacuum filtered and washed with 50 ml using a Whatman® grade 595 paper filter. The sample was kept in a vacuum oven at 60°C for 24 hours after which the sample was completely dry.

The second doping method is the loading in saturation, which is based on drug doping of diatom frustules by Gnanamoorthy et al. [58]. In this process a highly concentrated dopant is mixed with the frustules and evaporated, resulting in precipitation of the dopant onto the surface of the frustules. In our work $\text{Ce(NO}_3\text{)}_3$ is mixed with diatom frustules in a glass bottle with a proportion of 1.5 g $\text{Ce(NO}_3\text{)}_3$ per g diatom frustules, and water is added until a liquid solution is formed. The sample was placed on the shaking table at 320RPM for 72 hours. The solution was transferred to a round aluminium container and placed in an oven at 80°C under ambient atmosphere for 24 hours to completely dry the sample. The solid layer of $\text{Ce(NO}_3\text{)}_3$-containing diatom frustules was removed from the Al container and broken with the use of a glass stirring rod.
Chapter 2. Doping of diatoms frustules

The loading in saturation resulted in an excess of $\text{Ce(NO}_3\text{)}_3$ outside the frustules, binding them together and requiring an addition separation step. Moreover, for our proof of concept it is important to dope only the inside of the diatom frustules with corrosion inhibitors to prevent their chemical interactions with the coating. The third doping technique was prepared in order to reduce this amount of $\text{Ce(NO}_3\text{)}_3$ outside the frustules by a capillary loading method. In this technique 500 mg diatom frustules is mixed with 10 ml of 0.3 M $\text{Ce(NO}_3\text{)}_3$. This mixture is put inside a 50ml glass bottle at ambient temperature of 23°C in unstirred condition for 70 hours. A Whatman® grade 595 paper filter is placed inside the solution as shown in figure 2.6 in order to remove all the excess solution. In this way a moisture of diatom frustules remains in the beaker and the buildup of additional $\text{Ce(NO}_3\text{)}_3$ outside the frustules is reduced. The moisture is placed in a vacuum oven at 60°C for at least 24 hours to completely dry.

Figure 2.7 shows the SEM-EDX spectra for the previously discussed loading methods which were performed on acid treated diatom frustules. 3

Figure 2.7: SEM-EDX spectra for unloaded and loaded diatom frustules with $\text{Ce(NO}_3\text{)}_3$ using different loading methods.

Figure 2.7 shows that there are no traces of cerium present after the loading by dispersion at ambient temperature, indicating that the doping was ineffective or too scarce to detect. These result contradicts the work of other scientists who show that DE are effective adsorbents [85–88]. However, they used other metallic adsorbents and surface modified DE for better adsorption. Additionally, they extended their work on experimental conditions such as the solution pH and concentration of the adsorbents. In this study all these different conditions were not investigated. Alterations of the experimental conditions and using surface treated DE could change the outcome of the loading capabilities drastically. The SEM-EDX spectrum for the loading by dispersion at elevated temperature (60°C) also shows to be

3The spectra for the alkaline and acid + alkaline treated diatom frustules are similar and can be found in Appendix C.
an ineffective doping method. This proofs that chemically treated diatom frustules do not contain any cations with which the cerium can exchange with.

The loading by capillarity shows a different SEM-EDX spectrum compared to the loading by dispersion. Three apparent peaks for Cerium at 4.8 KeV \((Ce - L\alpha 1)\), 5.3 KeV \((Ce - L\beta 1)\) and 5.6 KeV \((Ce - L\alpha 2)\) are present, confirming that the doping method is effective. Quantitative calculations on 8 EDX measurements show that the diatom frustules contains 6 to 8 times more silicon than cerium (in weight). However, quantitative EDX measurement are not very accurate and the chemical composition remains unknown.

The highest amount of cerium is detected for the loading in saturation process, as can be seen in figure 2.7. In addition to the peaks present in the capillary loaded diatom frustules, two other higher energy peaks for cerium are present at 0.8 KeV \((Ce - M\alpha 1)\) and 6.0 KeV \((Ce - L\gamma 1)\). Quantitative calculations on 6 EDX measurements show that the diatom frustules contains between 0.7 and 1.3 times silicon with respect to cerium (in weight). In addition to EDS, also XRD measurements have been conducted on the loading by saturation loaded frustules. The spectra can be found in Appendix D. XRD shows that the cerium is present as Cerium nitrate hexahydrate \((Ce(NO_3)_3 \cdot 6H_2O)\) and the less hydrous tetraaquatris Cerium nitrate \((Ce(NO_3)_3 \cdot 4H_2O)\). This proofs that the loading method has not changed the chemical structure of the inhibitor and that the salt has simply precipitated during the process.

Figure 2.8 shows SEM images of the loading by saturation and capillarity loading methods.

![Figure 2.8: SEM images with scale bars for capillary loaded (top) and loading in saturation (bottom) on water separated diatom frustules (left) and wet chemistry treated diatom frustules (right), insets show high magnification images.](image)

The SEM images for diatom frustules loaded by capillarity do not show the presence of separate particles besides the diatom frustules. However, on higher magnification (inset) it can be seen that the small pores are partially covered with a layer of what appears to be cerium. No visual differences between water separated and wet chemistry treated diatom frustules (acid, alkali or acid + alkali) were found.

The SEM images for diatom frustules loaded in saturation show the abundant presence of \(Ce(NO_3)_3\). For the water separated diatom frustules it seems that large amounts of \(Ce(NO_3)_3\) is precipitated outside
the diatoms, connecting them together and forming aggregates. Aggregates are also formed in the case of the wet chemistry treated diatom frustules (acid, alkali and acid + alkali), but the amount of \( \text{Ce(NO}_3\text{)}\_3 \) seems to be less, although the same concentrations were used during the loading process, suggesting that more \( \text{Ce(NO}_3\text{)}\_3 \) is present inside the frustules.

In conclusion, The loading by capillarity is effective in loading diatom frustules with \( \text{Ce(NO}_3\text{)}\_3 \) without forming large \( \text{Ce(NO}_3\text{)}\_3 \) aggregates outside the frustules. However, the amount of \( \text{Ce(NO}_3\text{)}\_3 \) remains scarce. The highest amount of available \( \text{Ce(NO}_3\text{)}\_3 \) is achieved by loading in saturation, although much of it is precipitated outside the frustules. Furthermore, it seems that the chemical treatments decrease external precipitation, suggesting more \( \text{Ce(NO}_3\text{)}\_3 \) is present inside the frustules. Further research into the doping of only the inside cavity of diatoms is required, recommendations on this matter can be found in section 2.5.

2.3.2 Effect of corrosion inhibitor types

This section describes the loading in saturation method for several other potentially interesting corrosion inhibitors. This study has been performed primarily to proof if diatom frustules can be used as carrier for other inhibitors as well, thereby showing their broad use.

Lithium Chloride (LiCl) is used as alternative inorganic corrosion inhibitor because recent study has shown promising results for lithium salts as leachable corrosion inhibitors in organic coatings for the protection of AA2024-T3 [15]. Also two organic corrosion inhibitors have been investigated because they are environmentally friendly and give anodic protection via a hydrophobic film of absorbed molecules on the metal surface [89]. In this work sodium diethylidithiocarbamate (Na-DEDTC) [22], and sodium 2-Mercaptobenzothiazole (Na-2-MBT) [17] were used.

In this process 250 mg of diatom frustules is mixed with 375 mg corrosion inhibitor and 1 ml water acting as solvent. The solutions are placed on the shaking table at 320RPM for 72 hours. The solution is transferred to a round aluminium container and placed in an oven at 80\(^\circ\)C under ambient atmosphere for 24 hours. The solid layer of inhibitor-containing diatom frustules was removed from the Al container and broken with the use of a small metal spoon.

Figure 2.9 shows SEM images of the diatom frustules after the loading treatment for the three different inhibitors.

![Figure 2.9: Doping diatom frustules with the corrosion inhibitors (a) Lithium Chloride (LiCl), (b) Sodium-diethylidithiocarbamate (Na-DEDTC), and (c) Sodium 2-Mercaptobenzothiazole (Na-2-MBT).](image)

It can be seen in figure 2.9 that accumulation of corrosion inhibitors onto the surface of the silica frustules is present in all cases. However, the morphology of loading of each inhibitor is very different due to their chemical differences. It seems that LiCl is mainly present in the pores and on the surface of the frustules.
Na-DEDTC is present at the surface while the pores remain partially open. Na-2-MBT shows mainly plate-like layers of corrosion inhibitor, which are formed separately and on the outer surface of the frustules.

This superficial but important study proofs the broad use of diatom frustules because they can be loaded with other corrosion inhibitors besides $\text{Ce(NO}_3\text{)}_3$. This suggests that it might be possible to synthesize multiple doped systems (e.g. one corrosion inhibitors located inside the diatom and the other one at the pores) which give both cathodic and anodic corrosion protection from the same carrier [89].
2.4 Conclusion

In this chapter the doping of diatom frustules with corrosion inhibitors has been discussed. Pure and intact frustules were obtained from the DE DiaFil 525. This was done through a water separation process followed by chemical treatments (acid and/or alkaline) which resulted in pure diatom frustules with more open pores and a narrower particle size distribution compared to the as received DE. Several different loading methods were used to dope the diatom frustules with the corrosion inhibitor Ce(NO$_3$)$_3$. The best controllable and higher loading was achieved by evaporating the saturated corrosion inhibitor solution mixed with the diatom frustules, resulting in precipitation of Ce(NO$_3$)$_3$ onto the surface of the frustules and will be used in the remaining chapters. Preferably only the inside of the frustules contains Ce(NO$_3$)$_3$ to reduce inhibitor interactions with the surrounding coating when they are used in practice. This was not achieved by any of the doping methods. However, the SEM images show that the chemical treated frustules contain less Ce(NO$_3$)$_3$ at the outside of the frustules after loading, suggesting that there is more available at the inside.

Different types of corrosion inhibitor (i.e. LiCl, Na-DEDTC and Na-2-MBT) have been used to dope diatom frustules. The doping was in all cases successful and resulted in completely different morphologies compared to Ce(NO$_3$)$_3$. This suggests that different corrosion inhibitors could be loaded together at different locations of the frustule to create anodic and cathodic corrosion protection.

The work in this chapter shows that the doping of diatom frustules with corrosion inhibitors is possible and that further research has to be done to dope only the internal structure of the diatom frustules with corrosion inhibitors. The doping degree and release kinetics of the diatom frustules will be evaluated in the next chapter with the use of a new in-situ detection system.

2.5 Recommendations

The water separation method can be improved and shows the potential to separate diatom frustules on their size. This could be interesting for the study on the effect of carrier size for corrosion protection. Another improvement would be to scale up the process and use larger quantities of DE, because the current process requires 5 hours to clean only a couple of milligrams DE.

Furthermore, diatom frustules are an environmentally-friendly alternative to currently existent approaches besides of being cost effective. The use of chemical cleaning treatments should thereby be reduced whenever possible.

The most important recommendation is the development of better doping methods. The currently explored methods were sufficient for this feasibility study but far from ideal when they have to be used in coating systems with enhanced protection properties. The development should be focused on doping only the inside area of the diatom frustules or cleaning the outside (e.g. surface treatments) combined with applying a controlled release mechanism. The addition of zeolites during the doping process is discussed in Appendix E and shows the potential use of diatoms as carrier for corrosion inhibitor doped zeolites that can be used for controlled release systems. A follow-up on this would be to develop double doped systems where also organic inhibitors are used to finally end up with combined anodic/cathodic corrosion protection systems with triggered release mechanisms for long term corrosion protection.

In addition to the above points on the methods, the use of other diatom frustules is recommended. Most of the currently used diatom frustules do not contain their outer Cribrellum (nano-porous layer) anymore, probably because these were damaged during the extraction processes or were already deteriorated during the fossilization. This nano-porous layer could be of crucial importance for better doping and (controlled) release. The intact frustules could be obtained by cultivating our own diatom species in the lab, and would even result in some extra oxygen for our brains.
Chapter 3

Inhibitor release from carrier systems

In the previous chapter the corrosion inhibitors where successfully stored at the surface of diatom frustules. In this chapter the release of the corrosion inhibitor from the frustules is discussed before they will be implemented inside self-healing protective coatings. For this, a new method for measuring corrosion inhibitor release from carrier systems is presented. First the development of the novel in-situ release kinetics setup is discussed in section 3.1. The techniques behind the setup are shown, followed by an extensive validation procedure in section 3.1.2 to show its capabilities and limits. In section 3.2 the setup is used to show that inhibitor release from carrier systems can be measured by using the $Ce(NO_3)_3$ doped diatom frustules which were prepared as discussed in chapter 2. The final conclusion on the work is given in section 3.3 and the chapter ends with the recommendations in section 3.4.

3.1 Novel In-situ Release Kinetics Setup (InReK)

3.1.1 Technique

A novel In-situ Release Kinetics Setup (InReK) was developed in order to in-situ measure the release kinetics of stationary corrosion inhibitor loaded carrier systems. A schematic illustration of the InReK setup inside the UV/VIS spectrometer is shown in figure 3.1.

Figure 3.1: Schematics of the In-situ Release Kinetics Setup (InReK) illustrating the different types of release that can be measured, a,b) different release kinetics based on the dissolution rate and dispersion of the corrosion inhibitor, and c) on demand release.
Chapter 3. Inhibitor release from carrier systems

The InReK setup shown in figure 3.1 makes use of a UV/VIS spectrometer to measure the concentration of the released inhibitor in solution. The setup consists of two devises; (i) a stirring device fitted inside the spectrometer, (ii) a semipermeable membrane (paper filter) fitted to the sample holder (tea-bag concept). In principle, the InRek setup can also be used with other spectrometers as well (e.g. FTIR or Raman). The results from the processed data can also be seen in figure 3.1, which illustrates the different types of release that can be measured by the InRek setup (i.e. different release kinetics based on the dissolution rate and dispersion of the corrosion inhibitor (line a and b), and on demand release (line c)).

3.1.1.1 UV/VIS spectrometer

The concentration of certain materials can be analyzed with the use of UV/VIS spectroscopy by measuring the absorbance of visible (VIS) or ultraviolet (UV) light. For certain molecules the absorption of electromagnetic energy of VIS light (400-800 nm; 299-149 kJ · mol⁻¹) and UV light (200-400 nm; 595-299 kJ · mol⁻¹) is sufficient enough to promote ground state electrons (lowest vibrational state) towards an excited electron level. The energy-level at which this interaction occurs depends on the characteristics of the molecule. According to Beer-Lambert law (equation 3.1), this absorbance \(A\) is nothing else than the ratio between the intensity of incident monochromatic light \(I₀\) and the intensity of transmitted monochromatic light \(I₁\) on a logarithmic scale [90, p. 1-9].

\[
A = \log_{10} \frac{I₀}{I₁} = \varepsilon cd \tag{3.1}
\]

The Beer-Lambert law also states that the absorbance of a solution is directly proportional to the concentration \(c\) of the absorbing species in the solution with a material specific molar attenuation coefficient \(\varepsilon\) and the path length \(d\) as shown in equation 3.1 [91].

In this work a dual beam spectrometer (as shown in figure 3.1) is used for InReK setup, specifically the LAMBDA 35 UV/VIS System from PerkinElmer. The light from a deuterium lamp (UV range) and a tungsten halogen lamp (VIS range) is directed through a set of focusing mirrors and light filters towards a monochromator. This optical device separates the light with a wide range of wavelengths into narrower selectable band of wavelengths. The monochromatic light is then split into two parallel beams through a beam splitter. One beam passes through a reference cell and the other beam through the sample cell. The used cells, named cuvettes, have a path-length of 10mm and are made from quarts-glass, which is also transparent in the ultraviolet regions. The light intensities of both beams are finally measured by a photo diode, whereby the reference beam intensity is taken as 100% transmission. The measurement will finally display the ratio of the two beam intensities. By compiling this intensities at different wavelengths, a complete absorbance spectrum can be created. [90, p. 10-24]

Additionally, the changes in concentrations can be determined by repeatedly compiling the absorbance spectrum at specific intervals and process the change over time[90, p. 165-210].

3.1.1.2 Stirring device

The purpose of the InReK technique is to measure the release kinetics from inhibitor-containing carriers inside the cuvette cell of the UV/VIS spectrometer. In order to do this, it is crucial to understand which physical effects are taking place during the release measurements. One important effect is the transport of inhibitors in (aqueous) solutions. This transport occurs by advective and dispersive-diffusive processes. Dispersion is caused by the mass flow of the solution and occurs only in the presence of advective flow. Diffusion is driven by thermokinetics, differences in chemical potentials causes transport in order to reach an equilibrium state. The quantitative description of diffusion was derived by Adolf Fick (1855).
Chapter 3. Inhibitor release from carrier systems

Fick’s first law shows that the transport by diffusion under steady-state conditions is proportional to the concentration differences

\[ j = -D_0 \frac{dC}{dx} \]  

(3.2)

Where \( j \) is the mass flux in \( \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \), \( D_0 \) the diffusion coefficient in \( \text{m}^2 \cdot \text{s}^{-1} \), \( C \) the chemical concentration expressed in \( \text{mol} \cdot \text{m}^{-3} \) and \( x \) the distance. Normally, the diffusion coefficient of solutes in aqueous solution can be estimated by stokes-Einstein equation

\[ D_0 = \frac{kT}{6\pi\mu r_0} \]  

(3.3)

Where \( k \) is the Boltzmann constant \((1.38 \cdot 10^{-23} \cdot \text{JK}^{-1})\), \( T \) the absolute temperature in Kelvin, \( \mu \) the fluid viscosity \( (0.8937 \cdot 10^{-3} \text{ Pa} \cdot \text{s} \text{ for water at room temperature}) \) and \( r_0 \) the radius of the solute. Moreover, many inhibitors are released in an ionized form, which affects the diffusion. Ions will not diffuse as single atoms, but as hydrated ions. Additionally, electrostatic forces between the cation and anion interact in the diffusion process. This makes it difficult to accurately estimate the diffusion coefficient [92, p. 377-381]. As a rule of thumb, the diffusion coefficient for liquids is in the order of \( 10^{-9} \cdot \text{m}^2 \cdot \text{s}^{-1} \) [92, p. 309-320]. This means that dissolved inhibitor requires a diffusion time of several hours until the equilibrium state is reached inside the cuvette (the same concentration everywhere). These slow concentration changes were observed during the development of InReK and made it impossible to accurately measure the release kinetics from carriers systems. Because of this, stirring the solution was required to increasing the dispersion of inhibitor. In this way the transport of the solute will only take seconds, making it possible to measure other slower concentration changes. Figure 3.2 illustrates the InReK stirring device that was developed.

![Figure 3.2: Illustration of the InReK stirring device.](image)

The custom made stirring devices was designed and build inside the UV/VIS spectrometer. The stirring device can be seen in figure 3.2 and consists out of a mounting support with two 12-volt DC brushless 2-pin computer fans \((40\text{mm} \times 10\text{mm})\) connected (in series) to a variable power supply. Two neodymium magnets \((1\text{mm} \times 2\text{mm} \times 5\text{mm})\) were glued in the center of both rotors. The device was positioned inside the UV/VIS spectrometer, fitting precisely within the cavity underneath the cuvette sample holders. The computer fans were aligned in such a way that the magnets are located directly underneath the cuvettes, one for the reference and the other for the sample. When the power supply is turned on, the computer fans start to rotate. A small magnetic stirring bar (flea) located inside the solution of the cuvette will
start to rotate due to the magnetic field created by the magnets. In order to know the stirring speed, the computer fan was captured on video while turning at several different electrical potentials with a high speed camera (240 frames/second), which resulted in the following conversion equation

\[ U = -3 \cdot 10^{-7} \alpha^2 + 0.003\alpha + 1.2524 \quad \text{where} \quad 800 \text{ RPM} \leq \alpha \leq 2500 \text{ RPM} \]  

(3.4)

Where \( U \) is the electric potential energy in Volt and \( \alpha \) the rotation speed in RPM.

### 3.1.1.3 Semipermeable membrane

During the development of the InReK system, two additional challenges were encountered which obstructed the measurements of release kinetics from inhibitor-doped carriers. The first challenge was the carrier itself that obstruct the transmission of light through the cuvette, resulting in light scatter and inaccurate absorbance spectra. The second problem is caused by the implementation of the stirring device. The device increases the necessary solute dispersion, but also transports the carriers, thereby shifting the release time of solute from the carriers into the same timescale as the dispersion of the solute itself. Both changes were being addressed by the implementation of a semipermeable membrane. Figure 3.3 shows the InReK cuvette containing semipermeable membrane.

![Figure 3.3:](image)

In figure 3.3 it can be seen that a semipermeable membranes (paper filter) is positioned at the top of the cuvette, folded into a cone shape. The ideal location of the paper filter would have been on the bottom of the cuvette to avoid gravitational forces. However, this was not possible due to the presence of the stirring flea. The paper filters have a particle retention size close to the carrier size. In this way water and dissolved inhibitors are able to move through the filter while the carriers are not. The filter also obstructs the waterflow which results in carriers which stay in a stationary position.

Before the experiment, the cuvette is filled with an aqueous solution and the UV/VIS spectrometer is calibrated (zero-point absorbance). After running the measurement for 30 seconds, the paper filter cone containing inhibitor-doped carriers is positioned in the solution on top of the cuvette. The measurement records the absorbance at a specific wavelength every second and can be stopped whenever desired.

### 3.1.2 Validation

An extensive validation process has been conducted in order to gain more knowledge on the reproducibility of accurate results and the effects of the system devises (e.g. stirring, semipermeable membrane and the amount of sample inside the filter). Pure \( \text{Ce(NO}_3\text{)}_3 \) salt is used as benchmark and compared with diatom frustules contain 1.5 g \( \text{Ce(NO}_3\text{)}_3 \) per g frustule. Preliminary UV/VIS experiments have been executed to define the absorption peaks for \( \text{Ce(NO}_3\text{)}_3 \) and construct the calibration curve. The spectra and linear calibration curve are shown in Appendix F. The spectra show that the absorption peak at \( \lambda = 252 \text{ nm} \) results in a linear calibration curve that can be used for Beer-Lambert’s law (eq. 3.1) to obtain the concentration.
\[ A = 1.66C - 0.01 \quad 0 \leq A \leq 3 \] 

(3.5)

Where \( A \) is the absorbance and \( C \) the concentration of \( Ce(NO_3)_3 \) in \( mg \cdot ml^{-1} \). This means that the InReK setup is capable of measuring \( Ce(NO_3)_3 \) concentrations up to 2 \( mg \cdot ml^{-1} \) (4.6 \( \cdot 10^{-3} \) molar).

Figure 3.4 shows the InReK validation results calculated with the calibration curve as shown in Appendix F for \( Ce(NO_3)_3 \) conducted at \( \lambda = 252 \text{ nm} \) for measurements (a) without and (b) with stirring.

![Figure 3.4](image)

**Figure 3.4:** InReK validation results calculated with the calibration curve as shown in Appendix F for \( Ce(NO_3)_3 \) conducted at \( \lambda = 252 \text{ nm} \) for measurements (a) without and (b) with stirring.

For the measurements shown in figure 3.4 an amount of 3.4 mg \( Ce(NO_3)_3 \) and 3.9 ml of demineralized water was used, resulting in a theoretical maximum concentration of 0.9 \( mg \cdot ml^{-1} \) \( Ce(NO_3)_3 \). It can be seen that all the measurements converge towards a final plateau which corresponds with this theoretical maximum, meaning that 100% is released in solution. \( Ce(NO_3)_3 \) with stirring disabled shows a slow concentration increase that reaches its final plateau after 13 hours. This is in good agreement with the diffusion coefficient for liquids (10\(^{-9}\) \( m^2s^{-1} \)) which suggests that the measurement shows the time required to equally distribute the dissolved \( Ce(NO_3)_3 \) in solution by mainly diffusion processes.

\( Ce(NO_3)_3 \) without a filter and stirring enabled reaches its maximum concentration instantly. This indicates that the advective flow by the stirring device increases the dispersion of the solution and reaches equilibrium state in a matter of seconds (stirring works).

\( Ce(NO_3)_3 \) inside the filter with stirring enabled results in a slower concentration increase of the solution compared to \( Ce(NO_3)_3 \) without a filter. The filter acts as a barrier for advection around the \( Ce(NO_3)_3 \) inside the paper filter, keeping them stationary. The slower advection can also result in increased concentration of \( Ce(NO_3)_3 \) inside the filter, resulting in a slower dissolution rate when it reaches the solubility limit. However, \( Ce(NO_3)_3 \) has a very high solubility limit of 1754 g/L (25\(^{\circ}\)C), making this unlikely.

\( Diat – Ce(NO_3)_3 \) (diatom frustules loaded with \( Ce(NO_3)_3 \)) without a filter and stirring enabled shows a higher concentration than physically possible (>100% release). This is caused by the interference of the diatom frustules with the transmission of light. It can be seen that when stirring is disabled the absorbance returns towards the expected value (100% release), because the diatoms settle to the bottom of the cuvette.
\textit{Diat} – Ce(NO$_3$)$_3$ inside the filter with stirring enabled result in a similar release compared to Ce(NO$_3$)$_3$ inside the filter with stirring enabled. This indicates that the frustules are effectively held away from the light-beam while maintaining proper release. The small difference compared to pure Ce(NO$_3$)$_3$ could suggest that the diatom frustules do not significantly effect the release of Ce(NO$_3$)$_3$. However, it could also indicate the limitations and capabilities of the system (e.g. measurement accuracy) are responsible for the difference. Further validation of the system is required to explain the differences.

The above shown result illustrates the importance of the combined stirring device and semipermeable membrane and that measuring the release kinetics from inhibitor doped carriers is possible with the InReK setup. However, further validation of the InReK system is required to exclude other variables and take the accuracy and reproducibility of the method into account as will be seen in the next sections.

### 3.1.2.1 Reproducibility & accuracy of results

The accuracy and reproducibility of the InReK setup was determined by conducting the same experiment under the same conditions in threefold. The experiments were performed with 3.6 ± 0.2 mg pure Ce(NO$_3$)$_3$ and 3.8 ± 0.2 mg Ce(NO$_3$)$_3$ doped inside diatom frustules (6.3 ± 0.2 mg Diat – Ce(NO$_3$)$_3$). The ±0.2 mg is the accuracy of the laboratory balance and dosing precision. The InReK setup (rotating at 1400 rpm) started measuring and after 30 seconds the inhibitor (inside a Grade 1 paper filter) was placed on top of the cuvette, filled with demineralised water (3.9 ml). Figure 3.5 shows the results of the accuracy and reproducibility experiments.

![Figure 3.5: InReK threefold reproducibility & accuracy results for pure Ce(NO$_3$)$_3$ (black lines) and doped Diat – Ce(NO$_3$)$_3$ (red lines) conducted at $\lambda = 252$ nm for (a) the measured concentration and (b) release percentage after data handling with the error bars indicate the standard deviation.](image)

In figure 3.5(a) it can be seen that the theoretical amount of Ce(NO$_3$)$_3$ corresponds well with the measured release concentration of the solution after reaching a final plateau. The differences that are visible are most probably due to the preparation precision of the samples. If this is taken into account, all final plateaus can be seen as 100% release. However, the differences could also be caused by the accuracy of the UV/VIS spectrometer or the experimental setup.

Data handling techniques have been used to correctly calculate the accuracy of the release results, taken the precision of experimental preparations into account. This is done through the following steps:

- Reducing vibrational noises (high frequency fluctuations in the absorbance spectra) by averaging the datapoints (1s) with its 5s nearest neighbors.
Chapter 3. Inhibitor release from carrier systems

- Assigning the 100% release point to the highest absorbance point when the measurement reaches a plateau that agrees with the theoretical amount of \( \text{Ce(NO}_3\text{)}_3 \).
- Assigning the starting point for release when the concentration reaches 0.05% release. This is necessary because the initiation time (first 5 to 20 seconds before reaching 0.05% release) is influenced by the insertion-time of the sample inside the UV/VIS (which takes between 5 to 15 seconds), thereby not mainly depended on the release itself.
- Calculate the release times for 10%, 25%, 75%, 95% and 100% release, respectively.

Figure 3.5(b) shows the data from 3.5(a) after data-handling, including error-bars showing the standard deviation between the three samples. The lines are added for visualization purposes only. In the figure it can be seen that below 75% release, the measurements have a very high accuracy making the error bars barely visible. The accuracy of the measurement decreases above 75% due to the fact that the release reaches convergence, resulting in larger differences between the samples. From these results it can also be concluded that the measurements are reproducible because only small deviations between the measurements are present. However, one should be cautious when concluding about release times above 75%.

3.1.2.2 System variables

The system variables for the InReK system are a) stirring speed, b) amount of carriers and corrosion inhibitor inside the filter, and c) filter type. The influence of these variables can effect the validity of the release measurements. The effect of the system variables on the release measurements is evaluated by solely changing one system variable. The experiments are performed with pure \( \text{Ce(NO}_3\text{)}_3 \) and 1.5 g \( \text{Ce(NO}_3\text{)}_3 \) per g doped diatom frustules (Diat – \( \text{Ce(NO}_3\text{)}_3 \)) and will be discussed in the next sections.

a) Stirring speed

Figure 3.6 shows the effect of stirring speed at 800, 1400 and 1700 rpm on (a) release kinetics and (b) release time.

![Figure 3.6](image)

**Figure 3.6:** Effect of changing of stirring speed at 800, 1400 and 1700 rpm on (a) release kinetics and (b) release time. Error-bars show the measurement accuracy (based on section 3.1.2.1), lines are added for visualization purposes only.

It can be seen in figure 3.6 that increasing the stirring speed from 800 to 1400 rpm does not have any effect on the release time. This can be explained by the fact that the stirring speed between 800 and 1400 rpm results in adequately fast dispersion to overcome the slow diffusion processes of \( \text{Ce(NO}_3\text{)}_3 \) in
solution. However, the increase of stirring speed from 1400 rpm to 1800 rpm does result in a slightly faster release. Figure 3.7 illustrates the principle of changing the stirring speed on the waterflow to explain the faster release.

![Figure 3.7](image)

**Figure 3.7:** Graphical illustration of the effect of stirring speed on the water-flow inside the cuvette.

It can be seen in figure 3.7 that advection inside the filter occurs when the stirring speed is increased to 1700 rpm due to the increase in waterflow. This results in dispersion of the dopant inside the filter and thereby a faster release.

It should be noted that the changes in release times are relatively small and close to the accuracy of the measurement. There is a possibility that the accuracy of the system plays a significant role and more results are required to confirm the processes. Nevertheless, increasing the stirring speed above 1400 rpm seems unnecessary and is unwanted for stationary particle release measurements.

b) Amount of carriers and corrosion inhibitor inside the filter

Figure 3.8 shows the effect of changing the amount of $Ce(NO_3)_3$ inside the filter to 2.0, 3.5 and 5.5 mg on (a) release kinetics and (b) release time.

![Figure 3.8](image)

**Figure 3.8:** Effect of $Ce(NO_3)_3$ inside the filter at 2.0, 3.5 and 5.5 mg on (a) release kinetics and (b) release time. Error-bars show the measurement accuracy (based on section 3.1.2.1), lines are added for visualization purposes only.

It can be seen in figure 3.8 that the three pure $Ce(NO_3)_3$ samples with different amounts of inhibitor inside the filter result in the same release kinetics and time. This confirms the linear relationship between
the measured absorbance and calculated concentration through Beer-Lambert law (eq.3.1).
The results also show that the release time for the Ce(NO₃)₃ inside the diatom frustules (Diat – Ce(NO₃)₃)
is significantly longer compared to pure Ce(NO₃)₃. This can be explained by the fact that doped diatom frustules require more volume inside the filter to reach the equivalent amount of Ce(NO₃)₃ compared to the pure samples, resulting in a longer diffusion path and thereby a slower release. Moreover, the results in figure 3.8 show that a slower release is achieved by the 3.5 mg Diat – Ce(NO₃)₃ compared to the 2.0 mg Diat – Ce(NO₃)₃. Figure 3.9 illustrates the amount of corrosion inhibitor inside the filter located on top of the cuvette.

![Figure 3.9](image)

**Figure 3.9:** Graphical illustration of the amount of corrosion inhibitor inside the filter located on top of the cuvette.

It can be seen in figure 3.9 that a larger volume of corrosion inhibitor inside (V) the filter results in a longer diffusion path (r) and thereby in a slower release. However, the 5.0 mg Diat – Ce(NO₃)₃ sample shows a faster release compared to the 3.5 mg sample although the volume increased. The error-bars indicate that the difference between these two samples is smaller than the achieved accuracy by the InRek setup (based on the results in section 3.1.2.1). This means that there could be a change in release kinetics, but smaller than the accuracy of the measurement. Furthermore, the capillary effect of the paper filter could cause the water-level to drop below the sample, resulting in a slower release. However, visual inspection showed that the water-height after the measurements remained higher than the sample-height in all cases.

It can be concluded that only increasing the amount of Ce(NO₃)₃ inside the filter will not result in any changes in release kinetics while changing the amount of diatom frustule carriers loaded with Ce(NO₃)₃ does. However, higher accuracy is required (e.g. more samples) for determining the precise relationship between the amount of corrosion inhibitor inside the filter and the release kinetics.

c) Filter type

Table 3.1 shows the properties of the cellulose paper filters types that were used. Figure 3.10 shows the effect of changing the filter type on (a) release kinetics and (b) release time.

**Table 3.1:** Properties for cellulose paper filters from Whatman®

Source: [http://www.sigmaaldrich.com](http://www.sigmaaldrich.com)

<table>
<thead>
<tr>
<th>Particle retention size (µm)</th>
<th>Grade 595</th>
<th>Grade 1</th>
<th>Grade 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (µm)</td>
<td>4-7</td>
<td>11</td>
<td>20-25</td>
</tr>
<tr>
<td>Weight (g m⁻²)</td>
<td>150</td>
<td>180</td>
<td>205</td>
</tr>
<tr>
<td>Filtration speed (s 100 mL⁻¹ Herzberg)</td>
<td>80</td>
<td>150</td>
<td>37</td>
</tr>
</tbody>
</table>
Chapter 3. Inhibitor release from carrier systems

Figure 3.10: Effect of changing the filter type on (a) release kinetics and (b) release time. Error-bars show the measurement accuracy (based on section 3.1.2.1), lines are added for visualization purposes only.

The properties of the paper filter are explained briefly before the measurements can be discussed. The particle retention size for the paper filters defines the retention level when 98% of the total number of particles initially challenging the filter is obtained. The filtration speed of paper filters is defined with a Herzberg flow rate tester. Prefiltered deaerated water is applied to the test filter (effective area 10 cm²) at a constant hydrostatic head (10 cm). The rate of the flow is measured in seconds per 100 mL. In table 3.1 it can be seen that the particle retention size, filter thickness and filtration speed are not directly related to each other. For instance, the thicker Grade 1 filter has a slower filtration speed although its particle retention size is larger compared to the Grade 595 paper filter. Figure 3.11 shows a cross-sectional representation of the different paper filters and their properties.

From this illustration it becomes clear that the filtration speed is based on the combination of; (i) pore size, (ii) paper thickness, and (iii) pore distance (number of pores). If the pore distance becomes smaller, the length of the diffusion path will decrease, increasing the filtration speed.

From figure 3.10 it can be seen that pure and doped samples result in similar release kinetics (most likely an error due to convergence). The results also show that a paper filter with a higher filtration speed results in a faster release of the Ce(NO₃)₃ in solution.

In addition to the filtration speed, care must be taken on selecting the particle retention size. Small particles can penetrate the filter whereas bigger particles can block the pores of the filter when an improper particle retention size is selected. In the case for our diatom frustules (mean particle size of 11 µm), the Grade 1 or 595 paper filter would be the best choice. The particle retention size of these paper filters is close to the actual particle size and the filtration speed is adequately fast to measure the release kinetics of Ce(NO₃)₃ inside a paper filter under steady state conditions. However, it is crucial to
Chapter 3. Inhibitor release from carrier systems

state that the measured release kinetics by the InReK system will always be a combination of the paper filter filtration speed and actual release speed of the corrosion inhibitor inside the filter. This means that a reference sample (pure inhibitor) inside the same type of filter is required to measure the effect of the carrier on the release kinetics, which will be the difference in release kinetics between the reference and the carrier sample.

It can be concluded that solution stirring and adding a semipermeable membrane are crucial for the InReK setup. More detailed validation tests proofed that the release kinetic results are reproducible and that variances in stirring speed, sample size and filter type do not overtake or significantly effect the results. Pure $\text{Ce(NO}_3)_3$ shows a faster release than the doped systems in all cases, thereby confirming that the release kinetics from carrier system is indeed the primary transport system measured by the InReK setup.

The validation results are also used to select the following system settings to acquire the most reliable results on the release kinetics from diatom frustules carriers:

- Select a stirring speed between 800 and 1400 rpm to avoid slow diffusive processes by the solution or advection inside the filter.
- Prepare sample sizes around 3.5 mg $\text{Ce(NO}_3)_3$, which is a compromise between reducing the effect of sample preparation inaccuracies and large sample quantities.
- Use a Grade 1 or 595 type filter to avoid particles passing through the filter while maintaining an adequate filtration speed.
- Compare results with a reference sample containing an equivalent amount of pure $\text{Ce(NO}_3)_3$ if possible.
- Repeat the same measurement at least 3 times to achieve a better accuracy.
Chapter 3. Inhibitor release from carrier systems

3.2 Release kinetics from $\text{Ce(NO}_3\text{)}_3$ doped diatom frustules

In the previous section it was shown that the release kinetics of $\text{Ce(NO}_3\text{)}_3$ from doped diatom frustules is different compared to pure $\text{Ce(NO}_3\text{)}_3$. In this section the difference will be discussed in more detail to prove that the release from inhibitor carrier systems can be measured. The measurements in this section are performed on diatom frustules which were loaded with $\text{Ce(NO}_3\text{)}_3$ through the saturation method. The effect of using a different cleaning treatment and $\text{Ce(NO}_3\text{)}_3$ concentrations on the release kinetics will also be discussed.

Figure 3.12 shows the effect of changing (a) the diatom frustule cleaning treatments and (b) the amount of $\text{Ce(NO}_3\text{)}_3$ per diatom frustule on the release kinetics whereby pure $\text{Ce(NO}_3\text{)}_3$ is used as reference sample.

![Figure 3.12](image)

**Figure 3.12:** The effect of changing (a) diatom frustule cleaning treatments and (b) amount of $\text{Ce(NO}_3\text{)}_3$ per diatom frustule on the release kinetics whereby pure $\text{Ce(NO}_3\text{)}_3$ is used as reference sample. Error-bars show the standard deviation created by threefold sampling and the lines are added for visualization purposes only.

It can be seen in figure 3.12 that the release of $\text{Ce(NO}_3\text{)}_3$ from doped diatom frustules takes longer compared to pure $\text{Ce(NO}_3\text{)}_3$ while both have a similar trend and show full release. These similarities suggest that both systems have the same diffusion controlled (Fickian like) transport mechanism. The fast release of the pure $\text{Ce(NO}_3\text{)}_3$ shows that the salt has a high dissolution rate. The slower release from diatom frustules (while maintaining the same dissolution rate and transport mechanism) shows that the porous network of the diatom frustules changes the diffusion path. This suggests that the release kinetics can be altered by the frustule architecture (i.e. size and porosity). Furthermore, the fact that the InReK system is capable of in-situ measuring small differences in diffusion path with the use of a very soluble salt proofs that the release from inhibitor containing carriers can be measured with high accuracy and enables us to compare, quantify and understand the release kinetics from different carrier systems.

It can also be seen in figure 3.12(a) that the release of $\text{Ce(NO}_3\text{)}_3$ from chemically treated diatom frustules has a slower release compared to water separated frustules. However, the difference stays within the margin of error for the measurements and thereby suggests that the chemical treatment does not effect the release kinetics drastically.

From figure 3.12(b) it can be seen that diatom frustules which contain less $\text{Ce(NO}_3\text{)}_3$ result in a slower release. This result is in good agreement with the hypotheses that diatom frustules increase the diffusion paths and shows once more that is possible to measure small changes in the carrier system with the InReK setup.


3.3 Conclusion

In this chapter a new method for measuring the corrosion inhibitor release from carrier systems has been presented. The method makes use of a UV/VIS spectrometer by measuring the inhibitor concentration after release in solution and can be used with other types of spectrometric devices as well (e.g. IR or Raman).

The setup makes use of a stirring device and a semi-permeable membrane (paper filter). The stirring device is used to increase the dispersion of the released corrosion inhibitor in solution whereas the semi-permeable membrane is used to detain the carriers (tea-bag principle).

Extensive validation testing showed that the stirring and filter systems are required for accurately measuring the release kinetics. Changing the stirring speed and filter type does not significantly change the results, suggesting that they do not alter the transport mechanisms for release. The validation resulted in a list of settings in order to gain the most reliable and accurate results.

Finally the system was used to show the differences between the dissolution rate of pure \( \text{Ce(NO}_3\text{)}_3 \) and the release rate from doped diatom frustules containing different concentrations of \( \text{Ce(NO}_3\text{)}_3 \). The results show that the release rate of this inhibitor from frustule carriers is different than the dissolution rate, thereby suggesting that the release kinetics of corrosion inhibitor can be altered by the frustule carrier properties. In the next chapter, one diatom-doped system will be selected for further proof of the active corrosion protection in a coating system.

3.4 Recommendations

The most obvious recommendation is to actually use the InReK system where it was intended for. Investigate the effect of changing the carrier type, type of corrosion inhibitor, and doping methods on the release kinetics. The system also shows plenty of other opportunities where it can be useful. For instance, on measuring controlled release or the release of corrosion inhibitors from actual coating systems. Furthermore, the system shows a potential use for other applications as well (e.g. release by drug delivery systems).

There is also room for improvement on the InReK system itself. The biggest improvement would be to pump the solution through the spectrometer while keeping the rest of the setup outside the machine. This is interesting because it opens the possibility to;

- measure controlled release (e.g. adding chemicals for ion-exchange or pH),
- perform multiple measurements at the same time (e.g. electrochemical, spectroscopy and optical),
- use a micro-capillary device for single-particle analysis.

Especially the micro-capillary device combined with multiple in-situ measurements is very interesting because it will give us new and fundamental knowledge on single particles.
Chapter 4

Corrosion protection of coatings containing inhibitor doped diatom frustules

In the previous two chapters it has been shown that the corrosion inhibitor $\text{Ce(NO}_3\text{)}_3$ can be loaded and released from diatom frustules. In this chapter coatings containing inhibitor-doped diatom frustules are presented as the proof of concept that active corrosion protection can be realized. Furthermore, it will be the first time that diatom frustules are used as corrosion inhibitor carrier in coatings. $\text{Ce(NO}_3\text{)}_3$ is used as the corrosion inhibitor, epoxy as the coating matrix, AA2024-T3 as the substrate, and 0.05M NaCl as the electrolyte. The doping method for diatom frustules can be found in chapter 2. Figure 4.1 illustrates the model of the coating system evaluated in this chapter.

![Figure 4.1: Illustration of the corrosion protection mechanism of coatings containing inhibitor-doped diatom frustules.](image)

In figure 4.1 it can be seen how the active corrosion protection of coatings containing inhibitor-doped diatom frustules works. The cerium is released from the frustules and starts to form a protective insoluble hydroxide (or oxide) layer on the intermetallic compound phases (IMC) of the substrate when the scratch is exposed to the electrolyte.

In section 4.1 the preparation and characterization methods for the coatings are described. This is followed with section 4.2 on challenges during the coating production and the results and discussion on passive and active the corrosion protection when the frustule containing coatings are exposed to NaCl.
Chapter 4. Corrosion protection of coatings containing inhibitor doped diatom frustules

solutions. An adapted opto-electrochemical method combining electrochemical impedance spectroscopy (EIS) with online imaging has been used for this evaluation method. The final conclusion on the work is given in section 4.3 and the chapter ends with the recommendations in section 4.4.

4.1 Materials and methods

4.1.1 Materials

AA2024-T3 was used as metallic substrate. For the coating Epikote 828 & Ancamine 2500 were used, both supplied by Akzo Nobel. Xylene with a purity of 99% was used as epoxy solvent and purchased from J.T. Baker. Water separated diatom frustules as explained in section 2.2.1 were used as pigments. The corrosion inhibitor containing diatom frustules were loaded with $\text{Ce(NO}_3\text{)}_3$ through the saturation method described in section 2.3. NaCl with a purity of <98% was purchased from VWR Chemicals and used as electrolyte. All aqueous solutions were prepared using Milipore® Elix 3 UV filtered water.

4.1.2 Sample preparation

4.1.2.1 Substrate pre-treatments

Pre-treatments are carried out to achieve a controllable and reproducible passive layer on the aluminum substrates. The procedure was adopted from Ferrer et al. [22] to promote adhesion. Aluminum alloy AA2024-T3 with a thickness of 2 mm was cut into 50 mm x 25 mm sized samples with the use of a metal sheet cutter (Darley). The samples were first abraded with Scotch Brite 3M “Clean N Finish grade AVFN” and decreased with acetone. This was done to remove the top native oxide layer and create a good surface texture for the epoxy. The samples were then pre-treated in an alkaline aqueous solution of 2.0 M NaOH for 10 seconds followed by rinsing in water and air dried to increase the amount of hydroxyl groups ($\text{OH}^-$) on the surface [93].

4.1.2.2 Coating preparation

Several different preparation parameters have been used to optimize the quality of the coatings (e.g. types solvents and the mixing order, duration and speed). Here, only the final chosen parameters will be mentioned.

The coatings were prepared using the epoxy (Epikote 828) and amine cross-linker (Ancamine 2500) in 5:2.9 weight ratio to reach amine-hydrogen to epoxide stoichiometry. This was followed by adding 20 wt% Xylene in order to make the epoxy less viscous and reduce air-bubble entrapment in the coating. Xylene was chosen because it does not dissolve $\text{Ce(NO}_3\text{)}_3$ due to its nonpolarity [94], making it practically insoluble for hydrates [95]. The solution was shear mixed for 5 minutes at 2500 RPM in a high-speed mixer and pre-cured for 30 minutes at ambient conditions before the pigments (diatom frustules) were added. The pigments were first sieved with a 50 $\mu$m mesh sieve to reduce the number of aggregates before they were mixed with the epoxy. This mixing was done by hand to reduce the $\text{Ce(NO}_3\text{)}_3$ epoxy/amine interactions. The mixture was then applied to an AA2024-T3 sample with the use of a 100 $\mu$m spiral bar, followed by curing in an oven at 70°C for 72 hours.

Table 4.1 shows the compositions for the substrates after curing, which are discussed in this work. Figure 4.2 shows a schematic representation of the in table 4.1 presented coatings.

---

1 Later results have shown that chemically treated diatom frustules might have been a better choice because these diatoms contain less $\text{Ce(NO}_3\text{)}_3$ outside the frustules, as discussed in chapter 2

---

35
Table 4.1: Compositions for the coated substrates

<table>
<thead>
<tr>
<th>Code</th>
<th>PVC (%)</th>
<th>Corrosion inhibitor (g Ce(NO₃)₃ per g diatom frustules)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>0</td>
<td>0</td>
<td>120±10</td>
</tr>
<tr>
<td>ED</td>
<td>30</td>
<td>0</td>
<td>115±15</td>
</tr>
<tr>
<td>1.5Ce-ED</td>
<td>30</td>
<td>1.5</td>
<td>115±15</td>
</tr>
<tr>
<td>Primer+1.5Ce-ED</td>
<td>0+30</td>
<td>1.5</td>
<td>20±5+105±10</td>
</tr>
<tr>
<td>0.15Ce-ED</td>
<td>30</td>
<td>0.15</td>
<td>80±20</td>
</tr>
</tbody>
</table>

Figure 4.2: Schematic representation of the coating as presented in table 4.1

Table 4.1 presents five different coatings. Coating E is the reference sample only containing epoxy. Coating ED contains unloaded water separated diatom frustules. Three coatings contain water separated diatom frustules loaded with Ce(NO₃)₃; (i) 1.5Ce-ED containing 1.5 g Ce(NO₃)₃ per g diatom frustules (2.5 g contains 1.0 g diatoms and 1.5 g Ce(NO₃)₃), (ii) Primer+1.5Ce-ED containing a pre-cured 20±5 µm pure epoxy layer (primer) underneath the same 1.5Ce-ED coating, and (iii) 0.15Ce-ED containing a lower amount of 0.15 g Ce(NO₃)₃ per g diatom frustules. The pigment volume concentration (PVC) of diatom frustules was calculated as described in appendix G and is the same for all the pigment containing coatings.

4.1.2.3 Controlled damage

A 5 mm long scratch was created to test the corrosion protection of damaged coatings. The CSM micro-combi tester installed with a 41 µm thick Stanley knife tip was used, resulting in a scratch with of approximately 41 µm. The CSM tester is controlled through software (Scratch V4.37), which operates and records all the movements and applied forces. First, the profile of the coating was measured by conducting a pre-scan with a normal force of 0.03 N on the knife. After this, a scratch is created by applying a constant normal force on the knife with a speed of 2.0 mm/min. The penetration through the coating was confirmed by an electrical circuit between the AA2024-T3 substrate and the knife in series with an LED light.

Table 4.2 shows an overview of properties for the scratches that are discussed in this work.
Table 4.2: Scratch properties for the coatings used for the corrosion protection analysis

<table>
<thead>
<tr>
<th>Coating code</th>
<th>Applied force (N)</th>
<th>Coating thickness at scratch μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>4.0</td>
<td>121 ± 3.5</td>
</tr>
<tr>
<td>Primer+1.5Ce-ED</td>
<td>7.0</td>
<td>125 ± 5</td>
</tr>
<tr>
<td>0.15Ce-ED(1)</td>
<td>3.5</td>
<td>75 ± 5</td>
</tr>
<tr>
<td>0.15Ce-ED(2)</td>
<td>3.5</td>
<td>80 ± 3</td>
</tr>
</tbody>
</table>

From table 4.2 it can be seen that the variation of coating thickness at the scratch is smaller than the average coating thickness as shown in table 4.1. Additionally, thicker coatings and the addition of diatom frustules increase the required applied force for penetration.

4.1.3 Characterization

In-situ opto-electrochemical evaluation method

In this work, intact and damaged coatings were examined during long-term immersion tests in 0.05M NaCl solution up to 30 days. To monitor the corrosion behavior as function of immersion time, a novel in-situ opto-electrochemical evaluation technique\(^2\) was used for the evaluation of corrosion inhibiting species. This technique combines the traditional three-electrode electrochemical cell with a microscope camera and an image analysis program to online monitor the exposed coatings. Figure 4.3 shows the in-situ opto-electrochemical setup.

A USB microscope camera fitted with LED-lights was positioned in front of a transparent plexiglas screen, which is opposite to the coated sample surface. The camera is controlled through webcam software (JAWCAM V0.4.2.) which records and tags images every 600 seconds. Electrochemical Impedance Spectroscopy (EIS) and Open Circuit Potential (OCP) measurements are taken with the use of a potentiostat (Autolab PGSTAT 302N), which is connected to a three-electrode electrochemical cell, fitted inside a Faraday cage to avoid external interference. The electrochemical cell has a Ag/AgCl as reference electrode, 6.6 mm diameter platinum gauze as counter electrode and the coated AA2024-T3 sample as working electrode. The frequency range of study was \(10^5 - 10^{-2}\) Hz, with an applied amplitude of 10 mV (RMS) to minimize the influence of the test on the system while still obtaining a reliable response. The potentiostat is controlled with an USB interface through the software package NOVA V1.11.1 (Metrohm Autolab). Before initiating the first EIS measurement, the OCP of

\(^2\)The setup was initially developed by Christian Mathis (MSc. thesis project at NovAM in 2010) for in-situ evaluation of silane based healing agents for corrosion protection.
the system was recorded for 30 minutes. After this, a 10 minute OCP followed up by EIS measurements were executed hourly during the first 120 hours and every 5 hours after that.

To examine the coatings before and after immersion, optical microscopy (Keyence VHX-2000E) and field emission scanning electron microscopy (FESEM) (JEOL JSM-840) coupled with Energy Dispersive X-rays (EDX) spectroscopy for elemental analysis was used.

X-ray diffraction (XRD) was employed to analyze the chemical composition of the cerium nitrate hexahydrate $(\text{Ce(NO}_3)_3\cdot6\text{H}_2\text{O})$ doped diatoms inside the coating. For the measurements a Bruker D8 Advance diffractometer Bragg-Brentano geometry and Lynxeye position sensitive detector was used.
Chapter 4. Corrosion protection of coatings containing inhibitor doped diatom frustules

4.2 Results and Discussion

The results and discussion section contains three parts. In the first part the challenges during the coating production process are discussed. In the second part the passive corrosion protection is shown through the use of intact coatings. The last part discusses the active corrosion protection of damaged coatings through the use of the opto-electrochemical setup.

4.2.1 Challenges during the coating production

Several important observations were made during the preparation of the coatings. One of these observations was the color transition from clear transparent to yellow when the $\text{Ce(NO}_3\text{)}_3$ loaded diatom frustules were added to the epoxy amine. Figure 4.4 shows the final color of the coating after curing for (a) unloaded and (b) $\text{Ce(NO}_3\text{)}_3$ loaded diatom frustules.

![Figure 4.4: Coating after curing for (a) unloaded and (b) $\text{Ce(NO}_3\text{)}_3$ loaded diatom frustules.](image)

In chapter 2 it was shown that the doping techniques were not capable of loading only the internal structure of diatom frustules with corrosion inhibitors. The yellowing observed in figure 4.4 suggests that there are chemical reactions taking place between the ineffectively loaded $\text{Ce(NO}_3\text{)}_3$ and epoxy amine. Similar yellowing of epoxy by cerium salts were also observed by other scientists [96–100]. However, none of them could explain the precise reason of the reaction or reported any negative effect on the corrosion protection capabilities of the coating due to this yellowing. Some of the studies [96, 98, 100] couple the yellowing to the change of oxidation state for cerium from +3 to +4, into the formation of amorphous $\text{Ce}_2\text{O}_3$. In addition to the yellowing, cerium salts have been used as efficient catalyst for the ring opening of aromatic amines in epoxies [101]. In this case it is expected that the cerium-amine reaction also changes the structure of the polymer network, reducing the yellowing would in this case be beneficial for the quality of the coating.

In order to achieve this, several different preparation parameters were investigated. Pre-washing the $\text{Ce(NO}_3\text{)}_3$ loaded diatoms reduced the amount of $\text{Ce(NO}_3\text{)}_3$ per diatom but increased the yellowing, probably due to a better dispersion of the dissolved $\text{Ce(NO}_3\text{)}_3$ during the pre-washing. On the other hand, yellowing was reduced by using a non-polar xylene as epoxy solvent and by premixing this solvent with the epoxy and amine followed by pre-curing it for 30 minutes before the $\text{Ce(NO}_3\text{)}_3$ loaded diatoms were introduced by hand-mixing. Despite reducing the yellowing, none of these parameters could avoid the coloration completely.

XRD measurements have been conducted on coatings containing $\text{Ce(NO}_3\text{)}_3$ loaded frustules to further proof a change in the oxidation state for cerium. The spectra can be found in appendix D. The results showed that cerium could not be detected at all by XRD analysis due to the highly amorphous nature of the epoxy coating. This means that other ways have to be used for the identification of oxidation states and chemical compositions.

Because further investigation and improvement of the coating fell outside the scope and time of the project, the choice was made to continue the work with the preparation method as discussed in section 4.1.2.2, which resulted in the least yellowing.
Another challenge in the preparation of the coating was the homogeneous dispersion of frustule particles. The loading method resulted in (> 50 µm) clusters of frustules interconnected by Ce(NO₃)₃. To solve this initial challenge, the clusters were broken by forcing them through a sieve with a mesh size of 50 µm. Further inspection of the particles afterwards showed that most diatom frustules stayed intact after removing the clusters.

Visual and elemental inspection on the coatings containing Ce(NO₃)₃ loaded frustules was performed in order to locate the cerium, epoxy and frustules after curing. Figure 4.5 shows SEM image (a) of the coating containing Ce(NO₃)₃ loaded diatoms, (c) at higher magnification including an elemental line-mapping, together with the 2D elemental mappings (b) and (d) for Si, Ce and C.

![Figure 4.5: SEM image (a) of the coating containing Ce(NO₃)₃ loaded diatoms, (c) at higher magnification including an elemental line-mapping, together with the 2D elemental mappings (b) and (d) for Si, Ce and C.](image)

From figure 4.5 the presence of cerium inside, around and outside the silica frustule can be observed. The carbon in the system is due the presence of epoxy. The particle indicated with the arrow in figure 4.5(a) seems to be a precipitated cluster of cerium surrounded by epoxy. The yellowing of the coating confirms the presence of epoxy and cerium at the same location. Figure 4.5(c) shows the internal structure of a broken diatom that is filled and carbon rich. This was observed at several other broken and intact frustules as well. The presence of carbon inside the frustule suggests that the epoxy is capable of filling the internal structures. It seems that additional steps are required to prevent the epoxy inside the diatom frustules in order to minimize the epoxy/amine reaction.


Chapter 4. Corrosion protection of coatings containing inhibitor doped diatom frustules

4.2.2 Passive corrosion protection

A non-destructive test was used to know the quality of intact coatings as a function of immersion time. EIS measurements were performed on the coatings to obtain information (e.g. porosity, marcoscale defects and water permeation) that plays an important role for passive corrosion protection. Figure 4.6 shows the results via (a) impedance modules and (b) phase plots for intact epoxy coatings after 5h and 72h immersion in 0.05M NaCl.

![Figure 4.6: EIS results via (a) impedance modules and (b) phase plots for intact epoxy coatings after 5h and 72h immersion in 0.05M NaCl.](image)

From figure 4.6 it can be seen that both pure epoxy coating \(E\) and the coating with unloaded diatom frustules (\(ED\)) have very high total impedance\(^3\). This means the coatings are good barrier systems [102], even after 72h of immersion. The slight reduction of impedance for coating \(ED\) compared to \(E\) could be due to an increase in porosity [103] or the difference in the coating thickness.

On the other hand, the intact \(1.5Ce-ED\) coating (containing a high amount of 1.5 g Ce\((NO_3)_3\) per g diatom frustules) shows a much lower total impedance, typical for damaged coatings [102]. The change in phase for frequencies < 10Hz indicates the presence of an electrolyte pathway towards the metal substrate (e.g. poor barrier coating). The overall increase of total impedance after 72h immersion is the result of interdiffusive processes and the formation of an oxide layer on the surface of the aluminium substrate. The delamination of the coating and oxidation of the substrate after immersion were also confirmed by visual inspection after immersion. It seems that the \(1.5Ce-ED\) coating is highly porous, resulting in poor barrier properties. The porosity could be caused by the precipitated Ce\((NO_3)_3\) outside the diatoms, the higher amount of diatom aggregates which are promoted by adding more Ce\((NO_3)_3\), or the degradation of the epoxy due to the epoxy/amine reactions.

In order to produce coatings with a better passive corrosion protection within the time limits of the project, two additional coatings were prepared without changing the elements of composition. Coating \(0.15Ce-ED\) contains 10 times less Ce\((NO_3)_3\). It was prepared in order to minimize the Ce\((NO_3)_3\) outside the frustules and reduce the epoxy/amine interactions. It can be seen in figure 4.6 that the coating has good barrier properties. The drop in total impedance modules at low frequency is probably due to the fact that this coating is significantly thinner. Coating \(Primer+1.5Ce-ED\) contains a 20 \(\mu\m\) pure epoxy primer used to include a proper barrier and prevent delamination. The EIS results are identical to the unloaded diatom coating, showing that a good barrier was indeed achieved.

---

\(^3\)Impedance is close to the equipment measurement limitations.
4.2.3 Active corrosion protection

The active corrosion protection for two types of coatings containing diatom frustules loaded with $Ce(NO_3)_3$ are discussed in this section. Namely coating Primer+1.5Ce-ED and 0.15Ce-ED in duplo, which all showed good passive corrosion protection. The pure epoxy coating $E$ is used as reference. On each coating a similar 5 mm long scratch was created which was immersed in 0.05M NaCl solution up to 30 days. During this time of period, EIS and visual data were acquired through the use of the opto-electrochemical setup. The data was processed into videos showing the optical images of the scratch together with the total impedance modules, phase angle, and Nyquist plots simultaneously. These videos can be found in appendix H.

The EIS results are compared relative to each other in order to investigate the active corrosion protection. However, differences in thickness and composition between the samples will also affect the results and have to be taken into account. In general, the low frequency response relates to the charge transfer process at the solution-coating interface and active corrosion protection [104]. Because of this, the change in trend at low frequency is used in order to compare the EIS results. Figure 4.7 shows the total impedance modules and bode phase for the samples presenting the trends of change.

\[ \text{Figure 4.7: Bode and phase plots at the turning points of the low frequency bode modules evolution.} \]

The reference coating $E$ shows a significant increase of total impedance modules in the initial period, which happens at all frequencies. This increase is caused by the obstruction of diffusion pathways at

\[ ^4 \text{The results for sample ED were incomplete, otherwise this would have been a better choice as reference sample.} \]
the scratch and can be the result of scratch closing (coating relaxation) or the formation of insoluble oxides at the scratch surface. Instability of the system is shown by the drop in total impedance and phase angle followed by a slight increase again. Instability can be related to oxide repassivation at the exposed metal surface in/around the scratch or coating degradation (i.e. delamination, poor barrier properties), both affecting the diffusion pathways for electrolyte. However, the total impedance remains high at low frequency, suggesting that even without the available corrosion inhibitors there is some protection.

Coating Primer+1.5Ce-ED(1) contains a layer with corrosion inhibitors combined with a pure epoxy primer underneath. The EIS data shows the same trend for the total impedance modules as coating E but stability is increased (only small variations at the low frequency were detected). However, the trend for the phase modules is constantly decreasing and contains a second peak, which is opposite to coating E. These differences in stability and phase could be due to the presence of the corrosion inhibitor or the two-layer build-up of the coating.

Coating 0.15Ce-ED(1) contains a single layer with corrosion inhibitor. The total impedance modules is much lower compared to coating E, probably because the coating is much thinner. Furthermore, the total impedance modules shows almost no initial increase followed by a very large decrease which is opposite to coating E. This suggests that there is a significant loss of active or passive protection for some reason. Moreover, pitting processes can be detected by the small peak in phase angle at low frequency.

Coating 0.15Ce-ED(2) has the same compositions, thickness and scratch size as coating 0.15Ce-ED(1). However, the changes observed by EIS are completely opposite to each other and proof that corrosion behavior and/or EIS tests methods are very prone to local changes. This coating shows a larger increase of total impedance and phase modules compared to coating E, which is a strong indication that the corrosion inhibitor is actively protecting the scratch. Moreover, the initial increase takes place over a total duration of 27 days before it drops again, which is 13 times longer compared to the pure epoxy coating. Additionally, this sample was the only one showing a very stable phase for frequencies above 1Hz.

The change of the OCP and EIS over time for the different samples can also be compared to each other by plotting the data versus time. In this way also fast occurring phenomena can be detected. Figure 4.8 shows the acquired OCP during (a) the first 72 hours (b) up to 30 days and (c) the total impedance modules acquired at 0.01Hz up to 30 days.
Figure 4.8: Acquired OCP during (a) the first 72 hours up to (b) 30 days and (c) the total impedance bode modules acquired at 0.01Hz up to 30 days.

In figure 4.8(a) an initial stabilization time is visible for all the coatings. The OCP drops from -0.5 V and stabilizes at the OCP for bare AA2024-T3 of -0.7 V, consistent with previous reports for this material [105, 106]. Coating Primer+1.5Ce-ED(1) stabilizes within 4 hours, whereby all other samples require almost double that time. The OCP fluctuations during these first hours indicate pitting corrosion initiation and repassivation events at the exposed metal surface (scratch) [107]. This could mean that coating Primer+1.5Ce-ED(1) is less susceptible to pitting, possibly due to the presence of the corrosion inhibitor. From 12 hours of immersion onward, the OCP values for the 0.15Ce-ED samples starts to increase again (substrate becomes more catodic) while coating E and Primer+1.5Ce-ED(1) remain around -0.7 V. This could suggest that for samples 0.15Ce-ED the cerium cations are present at metal substrate and blocking anodic zones. This was also observed by Schem et al. [107] for CeO$_2$-filled sol-gel coatings on AA2024-T3 aluminum in 0.05 M NaCl after exactly the same immersion time. The OCP for sample 0.15Ce-ED(2) remains increasing until it starts to fluctuate after 32 hours of immersion. It becomes more complicated because also sample E starts to show an increase in OCP at 35 hours of immersion although there is no corrosion inhibitor available. This shows that protection is not the only possible explanation for increasing OCP, it could also be the result of dealloying anodic IMC phases and transforming them into cathodic zones.

Figure 4.8(b) shows that many different events are going on when longer immersion times are examined. For instance, sample E shows an ongoing increase of OCP from -0.7 V after 10 days. Sample 0.15Ce-ED(2) retains an OCP above -0.7 V until it drops after 27 days. Additionally, sample
Chapter 4. Corrosion protection of coatings containing inhibitor doped diatom frustules

0.15Ce-ED(2) shows large fluctuations around the second day of immersion. These fluctuations could be due to measurements faults but also due to oxidation and passivation processes. Comparing figure 4.8(b) with (c) shows that the OCP is similar to the total impedance modules acquired at 0.01 Hz for the inhibitor containing coatings. For sample E the impedance is much higher compared to the other samples opposite to the OCP values, possibly because the OCP measurements are not effected by the differences in thickness between the samples. The EIS and OCP measurements discussed above shows that the results remain open to interpretation. These measurements alone are unreliable to base conclusions on about the active corrosion protection. Other means are required to inspect active processes at the scratch during immersion.

The examination of the visual results gathered by the opto-electrochemical setup opened new pathways into understanding and interpreting the electrochemical results. The discussion below focuses on the interpretation of visual results and compare these to the EIS and OCP measurements in order to proof if there are signs of active corrosion protection by the corrosion inhibitor containing coatings. Figure 4.9 shows the scratched coatings during immersion in 0.05M NaCl inside the opto-electrochemical setup.

In figure 4.9 the delamination and corrosion events are indicated with arrows. The difference in color between sample 0.15Ce-ED(1) and 0.15Ce-ED(2) is due to another type of camera. The discussion below will also contain certain anomalies detected by the video results (Appendix H) which can not be made visible in figure 4.9 (e.g. formation of air-bubbles and delamination). For reference sample E, darkening of the substrate in/around the scratch combined with delamination directing away from the scratch happened within the first hours after immersion, indicating pitting at the
scratch combined with loss of adhesion. At the third day of immersion a large black spot forms (bottom of the scratch) followed by further delamination and blister formation. The color of the unprotected surfaces slowly blacken over time, indicating active underfilm corrosion. Correlating these results to the EIS and OCP data discussed earlier suggest that the increase of total impedance modules and OCP after 6 days of immersion is caused by the stagnation of delamination combined with the increase of oxides formation, thereby blocking the diffusion pathways for electrolyte towards the substrate.

The visual inspection for sample Primer+1.5Ce-ED(1) became a challenge due to the addition of a primer and the coloration of the toplayer caused by the Ce(NO$_3$)$_3$ and epoxy/amine interactions. Despite this, darkening of the scratch was visible from the start, similar to sample E. However, delamination did not occur within the first three days. This is considerably later compared to sample E and suggests protection by Ce(NO$_3$)$_3$. Moreover, differences in adhesion is an unlikely explanation for the later occurring delamination because both samples have the same substrate-interface. The point that the first delamination became visible (day 4) correlates exactly with the drop in total impedance and OCP and can thus be explained by the formation of unprotected area acting as additional diffusion pathways. Darkening of the delaminated area stagnates after 9 days and progressing delamination seems to take over after 10 days, again correlating with the changes in total Impedance modules and OCP.

The visual inspection of sample (0.15Ce-ED(1)) is remarkably similar to sample Primer+1.5Ce-ED(1), only now the delamination and coloration is much better visible. The similarities are the preliminary darkening around the scratch and the delamination that started from day 4. Also the trend for the (low frequency) total impedance modules and OCP for the two samples is similar, whereby the Primer+1.5Ce-ED(1) has the highest impedance due to its thickness. A difference in color can be seen by comparing the corroded areas of sample 0.15Ce-ED(1) with sample E. The unprotected areas without the corrosion inhibitor appear to be black compared to red for the Ce(NO$_3$)$_3$ containing coating. The difference in undercoating corrosion color could simply be caused by the yellow color of the coating. However, it could also be caused by a difference in chemical reactions of the electrolyte present at this location. [108] suggests that the red color is a result of replated copper. This is potentially interesting because a reasonable explanation could be that the available Ce$^{3+}$ in the electrolyte starts to form a passive layer at the IMC phases where the copper was dissolved, resulting in partial protection by the corrosion inhibitor causing the red color instead of black. Further analysis is required in order to proof this through.

In the case of sample 0.15Ce-ED(2), bubble formation and darkening of the scratch was observed during the first 16 hours. The bubble formation is a strong indication that oxygen reduction and the hydrogen evolution reactions take place at the substrate. However, only a very slowly darkening delamination region around the scratch start to appear. The delamination area becomes clearly visible after 9 days after which further darkening seems to stop. After 27 days of immersion the first rapidly growing delamination zone is observed. The combination of the visual proof that almost no delamination or underfilm corrosion is occurring during the first 27 days combined with the increased and stable total impedance modules and higher OCP value strengthen the suggestion that diatom frustules loaded with Ce(NO$_3$)$_3$ improve the active corrosion protection of the coating.
4.3 Conclusion

The preparation of coatings containing $\text{Ce(NO}_3\text{)}_3$-doped diatom frustules applied onto AA2024-T3 substrates was challenging but successful. Passive corrosion protection was initially not achieved due to an increase in coating porosity. This porosity was the result of $\text{Ce(NO}_3\text{)}_3$ precipitates outside the frustules, formation of frustule aggregates and possibly the chemical interactions between epoxy/amine and $\text{Ce(NO}_3\text{)}_3$. The amount of aggregates and $\text{Ce(NO}_3\text{)}_3$ precipitates lowered significantly by doping the frustules with a lower concentration of $\text{Ce(NO}_3\text{)}_3$ and sieving the inhibitor-doped frustules before mixing them with the epoxy/amine. Chemical interactions between epoxy/amine and $\text{Ce(NO}_3\text{)}_3$ were thereby also reduced but could not be prevented completely, resulting in yellowing of the coating. Two improved coatings were prepared which had good passive corrosion protection, similar to inhibitor-free coatings. These improved coatings were used in the proof of concept that inhibitor-doped diatom frustules can be used for active corrosion protection. Evaluation of the exposed damaged coatings with the in-situ opto-electrochemical technique showed to be mandatory for the correct interpretation of the EIS and OCP measurements. Although the tests appear to be very prone to local changes, all the inhibitor-doped diatom frustules coatings showed a prolonged corrosion protection compared to the coating without any corrosion inhibitor.

There are definitely signs of active-corrosion protection when inhibitor-doped diatom frustules are used inside the coating. The fact that this is achieved with coatings that are far from perfect and without controlled release proofs the feasibility of the concept but also emphasize the required steps to create a system that shows better active-protection compared to the currently available systems. In the next chapter a modeling approach will be described to advice on the best possible carrier geometry for active corrosion protection and establish the first steps to the theoretical limits of the concept.

4.4 Recommendations

The coatings prepared in this work were acceptable for the proof of concept but far from perfect. The thickness of the coatings should be controlled better and ideally be much thinner ($< 50\mu\text{m}$ thick). Also delamination should be prevented by optimizing the adhesion (e.g. adding adhesives, optimizing pre-treatments) and damage control can be improved. These improvements stabilize the exposed area of the substrate during the electrochemical measurements, making the corrosion activities at the scratch better detectable. Furthermore, the interaction between the epoxy/amine and the $\text{Ce(NO}_3\text{)}_3$ should be prevented. This could be done by selecting a corrosion inhibitor which does not interact with the polymer. Another option would be to use advanced doping techniques capable of loading only the inside of the frustules (e.g. electrodeposition, vacuum-drying or surface treatments) combined with frustule encapsulation (e.g. monomer deposition) or controlled release (e.g. ion-exchange).

The importance of using the in-situ opto-electrochemical evaluation method became undoubtedly clear in this work. I would recommend to always use visual monitoring during electrochemical measurements. Moreover, improving the pixel density by using better USB camera-microscope systems, further automatize the process, and using a multiplex system would definitely improve the quality and quantity of the results. Also the incorporation of IRR or X-ray combined with local electrochemistry (e.g. micro electrochemical systems) could be potentially interesting.

It is also important to state that the work in this study is not yet finished. More information and knowledge should still be gained on the discussed samples to really understand what is happening. It is recommended to inspect the exposed areas of the substrates by SEM-EDX and the electrolyte through ICP-OES. These techniques can be used to confirm the presence of the corrosion inhibitor and see if there are differences in the corrosion behavior. Furthermore, the use of other techniques such as SVET and X-ray tomography could also be used to gain more knowledge.
Chapter 5

Effect of carrier geometry & size on the corrosion inhibitor release: a modeling approach

The foregoing chapters have shown that inhibitor-doped diatom frustules can be used for active corrosion protection. However, the benefits for using frustules by their architecture and biodiversity has not yet been investigated. For this, a particle packing modeling approach will be presented in this chapter to study the influence of carrier geometry and size on the concentration of released corrosion inhibitor at scratches of different widths ($f(dx)$). In section 5.1 two particle packing algorithms are introduced. The first algorithm was written from scratch while the second one was already developed and will be used for our further work. In section 5.2 the translation from the algorithm to the simulation is made by showing the boundary conditions and the different particle shapes and sizes that will be used. Section 5.3 describes how the simulated conditions are applied to the algorithms and which steps were taken to correctly obtain the required data, including a mathematical representation for a damaged coating in corrosive environment. In section 5.4 the results on the influence of carrier shape and size on the concentration of released corrosion inhibitor at scratches of different widths ($f(dx)$) are shown and discussed. The chapter ends with the final conclusions on the work in section 5.5, followed with the recommendations in section 5.6.

5.1 Particle packing algorithms

In this section two different particle packing algorithms are discussed. The principle of both algorithms is the same, filling a volume in space (called a box) with randomly arranged particles, which can be in contact with each other, but are not allowed to intersect. The first algorithm is self-made and can be used to pack 3D spherical particles through static triangulation techniques combined with a trial-and-error approach. Although this first approach showed the capabilities of modeling, it was found that the limitations of this algorithm were too big, and thereby not capable for modeling the effect of shape and size of carriers on the release at a damaged coating. The second algorithms is the work of Amadio [109], who developed a new high-performance source code for the random packing of polyhedral particles at the university of Illinois (US). This algorithm better met our requirements for the model and is described in section 5.1.2.
5.1.1 V1.0: Packing of spheres through static triangulation techniques

The first algorithm (V1.0) was developed from scratch in MatLab R2014b. The model generates spherical packings effectively inside a periodic box for low packing fractions ($< 0.3$). Figure 5.1 shows the flowchart for the computational algorithm.

![Flowchart of the parking algorithm](image)

In the first part of the algorithm, a 3D numerical box is created and its volume is calculated. The number of particles is determined through the input data (i.e., particle size, size distribution and the packing fraction). In the next step of the code, random points inside the box are generated for each particle in the Cartesian coordination system. A Delaunay triangulation (tetrahedral mesh) is created around each point to ensure that the circumcircle associated with each triangle contains no other point in its interior \[110\]. The distance to the nearest neighbor is evaluated and set as the maximum radial size for the particle. Spheres are generated inside the Delaunay domains and the model is checked for overlapping spheres. New points are repeatedly generated if overlap exists. The algorithm ends when there occurs no overlapping and a datafile is created containing the calculated coordinates and input data. This can be used to plot the spheres with simulated radii in 3D space, with their center at the coordinate point. The complete algorithm can be found in appendix I.

The simplicity of the algorithm also has its limitations. Only the packing of spherical particles is possible with Delaunay triangulations. Furthermore, only low packing fractions can be computed due to the exponential increase in overlapping errors for higher packing fractions. Finally, the code is only capable of running small systems ($< 10^3$ particles), after which the computing time becomes a problem. These limitations of the algorithm made it impossible to study the effect of particle shape and size on realistically modeled anti-corrosion coatings. More advanced methods are required, e.g., using translation and rotational particle displacements techniques and Monte Carlo simulations. The development of such a code lies outside the time-frame of this project and it was decided to look for existing particle packing algorithms as discussed in section 5.1.2.
Chapter 5. Effect of carrier geometry & size on the corrosion inhibitor release: a modeling approach

5.1.2 V2.0: Packing of polyhedra through event-driven molecular dynamics and Monte Carlo displacement techniques

The second simulation algorithm (V2.0) is the particle packing code called Rocpack, developed at the faculty of Aerospace Engineering, University of Illinois (US), and runs on Linux systems. The source code is written in C++ and was originally build to simulate the microstructure of solid rocket propellants. The source code simulates dense packing of spheres and any other kind of polydisperse convex particles on systems containing up to $10^7$ particles. The source code uses a hybrid of two different packing algorithms, the Lubachevsky-Stillinger [111] (LS) and Monte Carlo trial displacement algorithm. The shape of the particle is defined with a list of indexed vertices and faces. The particles start as infinitesimal points in space and are distributed randomly within a given box. The particles are allowed to grow in time until the desired packing fraction is reached or until they tend to overlap each other (particle jamming), this method is called a time-driven process. The LS packing algorithm allows the particles to undergo elastic collisions with other particles when they grow. The LS algorithm is thereby called an event-driven process, because each change of state by the collisions is a separate event. Event-driven molecular dynamics (EDMD) algorithms are in general more effective in packing spheres than time driven algorithms, and represent physical processes such as the movement of liquids, gasses and crystals more realistically. However, when more complex particle shapes are used (multidimensional polyhedral bodies) the algorithm slows down substantially, because the collision responses between particles become more complicated. Additionally, the sharp edges of these particles cause the algorithm to run into numerical infinities thereby causing errors. These problems are tackled by interchanging the elastic collisions by Monte Carlo trial displacement techniques. In contrast to the LS algorithm, the particles are not allowed to move, but grow at a fixed location until overlap is about to occur. The colliding particles in question are now removed and new locations are looked for through computing trail displacements of the particles, until one is found that delays the collision event. During the process the dislocations which were not suitable are queued and used during the next dislocation event, which improves the efficiency of the Monte Carlo algorithm significantly. In the case no better location can be found for the colliding particles, the algorithm also displaces the neighboring particles, in order to avoid the system to get stuck (local jamming). This displacement process leads to a much more simplistic mathematical process because the particles stay in static conditions. It makes it easier to compute collisions through boolean values and thereby making the algorithm less prone to jamming when complex particle shapes are simulated.

The capabilities of this algorithm shows its potential use for our study on modeling the effect of particle shape and size on the protection area of anti-corrosion coating systems. Therefore, this algorithm will be used for our own work as discussed in the subsequent chapters.
5.2 Modeling particle-containing coatings

A crucial step of this modeling process is the translation of particle packing models into realistically simulated coating models to obtain useful information. In this section, the boundary conditions, particle shapes and sizes are discussed in order to obtain valid results on the effect of changing the particle shape and size on the released amount of corrosion inhibitor at scratches of different widths ($f(dx)$).

5.2.1 Boundary conditions

The following boundary conditions are required to accurately simulate a coating system containing carriers (particles) with corrosion inhibitor. First of all, the modeled section of the coating was defined as a box. The complete thickness of the coating had to be modeled in order to pack large particles in a realistic way. Obviously, the other dimensions have to be larger than the thickness and small enough to increase simulation time. The box dimensions [500 100 200] were found to be adequately fast for all simulated models, which resembles a 500 $\mu m$ by 200 $\mu m$ section of a 100 $\mu m$ thick coating in our model. The box is simulated under periodic boundary conditions. This means that the particles are allowed to move partly through the walls of the box, thereby approximating a larger (infinite) system [112]. Although the periodic condition is not correct for the coating-substrate boundary, it remains more realistic and accurate than solid boundary conditions. For the particles a pigment volume concentration (PVC) of 30% was chosen, as it is a realistic quantity for carriers containing corrosion inhibitors. Finally, making a coating with particles larger than half the coating thickness is not realistic due to mono-layers that start to form. For this reason the maximum particle size was set on 50 (resembling 50 $\mu m$ in diameter), independently of its geometry.

5.2.2 Particle geometries

Different convex polyhedral geometries have been modeled, which can be placed in two categories. Shapes with a uni-dimensional dependency, meaning that the size of the polyhedral only depends on variable. Secondly, shapes with multi-dimensional dependencies, whereby 2 or 3 variables are defined through the use of an aspect ratio.

5.2.2.1 Uni-dimensional dependent shapes

Spheres

Although the source code only supports convex polyhedra, one exception is made for spheres, due to the fact that the sphere was the original shape used in the LS algorithm [111].

Platonic solids

Platonic solids have equivalent faces composed of congruent convex regular polygons, meaning that all sides have the same length which are symmetrically bound to one common center [113]. Figure 5.2 shows the platonic solids used in the model. The geometrical formulas can be found in appendix J.

![Figure 5.2: Platonic solids.](image)
Archimedean solids

Archimedean solids consist similarly to platonic solids out of convex regular polygons. However, instead of one type of polygon for platonic solids, two or more types are arranged in the same way about each vertex whereby all sides have equal length [114]. Figure 5.3 shows the Archimedean solids used in the model. The geometrical formulas can be found in appendix J.

5.2.2.2 Multi-dimensional dependent shapes

Cylinders

Cylinders are modeled because this shape has the best resemblance with the diatom frustules used as corrosion inhibitor carriers as discussed in chapter 2 of this work. Cylinders also resemble other frustule shapes of the diatom family. However, a cylinder is not a polyhedron because its lateral surface is not a plane and it does not consist out of faces and vertices. In order to simulate cylinders, a prism with a 25-sided polygonal base is used. Although more faces result in a better representation of a cylinder, it also requires more processing time due to the increase of edges. Different aspect ratios were modeled, meaning the ratio between the base diameter \(d\) and height \(h\), resulting in rods \((h > d)\) and disks \((h < d)\). A maximum aspect ratio for the rod of \([1:7.5]\) and the disk of \([24:1]\) was reached, after which the computational time and boundary conditions became an issue. Figure 5.4 shows the cylindrical shapes with different aspect ratios.
Chapter 5. Effect of carrier geometry & size on the corrosion inhibitor release: a modeling approach

Figure 5.4: Cylindrical shapes with different aspect ratios.

Cuboids
Cuboids are also known as rectangular boxes. The unit size cuboid is equal to a hexahedron or cube (platonic solid) whereby the lengths of all the sides are equal \([a=b=c]\) as shown in figure 5.5. Polygonal cuboids are also similar to the modeled polygonal cylinders because a prism is used, only now with a 4-sided polygonal base. In this work, a cuboid is called a bar if the height is larger or equal than the width and larger than the depth \((c \geq a, c > b)\) and a sheet when the height is smaller than the width and depth \((c < a, c < b)\). Different aspect ratios were modeled, whereby maximum aspect ratios for the bar of \([1:1:8]\) and for the sheet of \([12:12:1]\) were reached. 5.5 shows the cuboids shapes with different aspect ratios.

Figure 5.5: Cuboids.

5.2.3 Particle sizes
The source code is volume dependent, meaning that the modeled particles always have the same volume (or distribution of volumes) independent of their geometry, which is defined in the code by the volume fraction of particles. With the use of the boundary conditions, the total box volume of \(1 \cdot 10^{-12} \ m^3\) and PVC of 30% result in a total pigment volume of \(3 \cdot 10^{-13} \ m^3\). Geometrical formulas for the shapes were used to find the particle size to volume relationship. Finally, models were created with a maximum of \(10^5\), and a minimum of \(10^2\) particles, resulting in particle sizes between 1 \(\mu m\) and 50 \(\mu m\), also depending on their shape.
Chapter 5. Effect of carrier geometry & size on the corrosion inhibitor release: a modeling approach

5.3 Model analysis

Our own modeling conditions as discussed in previous section were created and inserted into the packing algorithm (V2.0). Models were created with different shaped and sized particles, resulting in more than 1000 different models. This section of the thesis explains how the received model data was handled and analyzed to study the effect of different parameters on the inhibitor release. First, the data handling for one of the models containing 100 cubical particles is shown, followed by the mathematical representation of a damaged coating in a corrosive environment in section 5.3.2.

5.3.1 Data-handling for particle packing models

The particle packing source code is started through a simple command-line in the unix terminal. The code gains excesses to a file containing the input parameters and the shape of the particle as a list of indexed vertices and faces. When the code finishes (reached its desired packing fraction) an output file is generated. A snippet of the output file is illustrated below:

```plaintext
1 set packing_fraction = 0.30;
2 boundary { box 5.0 1.0 2.0 periodic }
3
4 cube {
5     translate < 1.93769956, 0.21191816, 0.56293899>
6     rotate <-0.96835697, 0.23176748, 0.09256634> 131.97796631
7     scale 0.08660323 color 0.500000 0.200000 0.200000 tag 0
8 }
9
10 cube {
11     translate <-0.88047224, 0.22748958, -0.27397922>
12     rotate < 0.61827761, 0.00518125, -0.78594267> 102.17983246
13     scale 0.08660323 color 0.500000 0.200000 0.200000 tag 0
14 }
15
16 cube {...
```

The first 3 lines of the output file show the input parameters (i.e. packing fraction and box size). This is followed by a listing of the modeled particle parameters. Each particle is translated in space on its center-point and rotated around its axes, resulting in a specific location where it does not overlap other particles. The scale and predefined color (RGB digits) is mentioned followed by a tag which is used when multiple shapes are present in the same model.

Figure 5.6 shows the simulation process that is used gain the particle data.
Figure 5.6: Simulation process that is used gain the particle data.

The output file can be read by an open graphics library (OpenGL), which is capable of rendering the particles into a 3D vector graphics as shown in figure 5.6(a).

The output file can also be converted into a binary mesh format. This is a standardized format used to save arbitrary multi-dimensional arrays into one file. The format is especially efficient for tomography studies whereas 2D images (slices) are generated from 3D data. Slices of the 3D packing can easily be obtained through the use of this binary file. A plane is specified by setting one of the axis as constant, resulting in particles that are cut through one plane. This can again be rendered through the use of an
openGL interface as shown in figure 5.6(b) for a single slice. A shell script was written (see appendix K) to create 10 different output-files and create 9 slices per output file, resulting in 90 slices in total per particle type. These sliced images are then processed through the use of ImageJ, a Java-based image processing program. Appendix L shows the code that was written to automate the image processing. The code locates the import and export directories, followed by converting the images to 8-bit in order to reduce processing power. The background is removed and converted to a binary mask, resulting in an image with foreground 255 (black) and background 0 (white), whereby all open particles are closed off (filling holes). A scale was set based on the pixel/model-size relationship. The particles can now be analyzed by ImageJ, whereby particles area smaller than 0.1 $\mu m^2$ were excluded to avoid particle splitting at intersections. The result is shown in 5.6(c) including the particle-numbering for one slice. Information of each particle is saved (e.g. particle size, and area) as shown in figure 5.6(e). Also as summarized report is saved (e.g. area percentage and the total number of particles) per slice as shown in figure 5.6(f). Finally, a script was written in visual basic to automatically build a hierarchical database containing the information for all the models together including the mean and standard deviation of particles per particle type. The final results can be found in appendix M.

5.3.2 Mathematical representation for a damaged coating in corrosive environment

Figure 5.7 represents a coating that is damaged followed by filling the damage with electrolyte.

![Graphical representation of a coating that is damaged, followed by filling the damage with electrolyte.](image)

In this work a scratch shown in figure 5.7 is represented mathematically, whereby two sides of the damaged coating will expose a number of particles ($N_P$) per $mm^2$ each having a volume ($V_P$). The number of particles was calculated by the particle packing analysis as discussed in the previous section. Based on the fact that the conditional probability distribution of dissecting a single particle once is 0.5 the simplification is made with the use of the statistical law of large numbers that all the dissected particle together contain half of the total volume. The total volume of exposed particles at the damaged surface ($V_{P,total}$) is thus

$$V_{P,total} = \frac{1}{2} N_P V_P \cdot 2(y \cdot z) = N_P V_P (y \cdot z)$$

(5.1)

The volume of electrolyte ($V_E$) that is present in the scratch is assumed to be equal to the total volume created by the scratch as shown in figure 5.7.

$$V_E = dx \cdot y \cdot z$$

(5.2)

In addition to this, only a fraction of the particle volume ($\phi_I$) relates to the corrosion inhibitor that can be released. The concentration of released corrosion inhibitor in the electrolyte can be calculated by multiplying the volume fraction of corrosion inhibitor per particle by the total volume of particles (equation 5.1) divided by the total volume of electrolyte (equation 5.2). This results in the following equation

...
Chapter 5. Effect of carrier geometry & size on the corrosion inhibitor release: a modeling approach

\[ C_i = \frac{\phi_I \cdot V_{P\text{total}}}{V_E} \rho_i = \frac{\phi_I \cdot V_P N_P}{dx} \rho_i \]  

(5.3)

where the density of the corrosion inhibitor \( (\rho_i) \) is expressed in \( mg \cdot mm^{-3} \) and the concentration in \( g \cdot ml^{-1} \).

In this study the corrosion inhibiting salt Ce\((NO_3)_3\) will be used inside the particles. The released concentration of Ce\(^{+3}\) from the particles results in the protection. Ferrer et al. [22] showed that zeolite carriers can release up to 4 vol% Ce\(^{+3}\) (based on 0.112 g Ce\(^{+3}\) per g zeolite). In chapter 3 it is shown that diatom frustules can release up to 12 vol% Ce\(^{+3}\) (based on 1.5 g Ce\((NO_3)_3\) per g frustule). However, these values are based on freestanding particles and not from exposed particles inside the coating. Based on this information, an amount of 5 vol% of Ce\(^{+3}\) is assumed to be released per particle (\( \phi_I = 0.05 \)) in this study. Ce\(^{+3}\) has a molecular weight of 140.12 g \( \cdot \) mol\(^{-1} \) and density of \( 6.77 \cdot 10^{-3} g \cdot mm^{-3} \).

Jakab et al. [115] showed that a concentration of Ce\(^{+3}\) between \( 10^{-4} M \) and \( 10^{-3} M \) is required for corrosion protection of AA2024-T3. These values are used in analysis of the data as threshold concentrations for protection. Rewriting equation 5.3 including the above parameters results in the minimum and maximum scratch size that can be protected as function of the number and volume of particles available at the scratch:

\[ 2.42 \cdot 10^3 \cdot V_P N_P < dx < 2.42 \cdot 10^4 \cdot V_P N_P \]  

(5.4)

Where the particle volume \( (V_P) \) is expressed in \( mm^3 \), the number of particles per unit area \( (N_P) \) in \( mm^{-2} \), and the scratch size \( (dx) \) in \( mm \). This relation will be used to compare the coatings with particles with different shapes and sizes.

\(^1\)Conversion from weight to volume percentage for diatom frustules can be found in appendix G.
5.4 Results and discussion

5.4.1 Effect of carrier shape on the corrosion inhibitor release concentration

The effect of the particle shape on the corrosion inhibitor release concentration is evaluated by modeling a box filled with particles. The boundary conditions (i.e. box size, wall conditions and PVC) are explained in section 5.2.1. Each model contains 3000 particles, which means that each particle has an uniform volume \( V_p \) of 10\(^3 \) \( \mu m^3 \) independently of the shape. The model is repeated 10 times for a particular particle shape that is discussed in section 5.2.2. This model is dissected 9 times in the xy-plane, resulting in 90 slices of 500 \( \mu m \) by 100 \( \mu m \) per particle shape. The number of particles \( N_p \) per mm\(^2 \) is calculated for each slice as explained in section 5.3.1. The average number of particles is used to calculate the scratch size \( (dx) \) through equation 5.4 as discussed in section 5.3.2. The first section discusses the effect of changing the particle shape for uni-dimensional shapes and the second section for multi-dimensional shapes using different aspect ratios.

5.4.1.1 Uni-dimensional dependent shapes

Figure 5.8 shows the effect of using uni-dimensional platonic, archimedean and spherical solids on the concentration of released corrosion inhibitor of scratches of different widths \( (f(dx)) \). Each bar in the graph represents the allowed scratch size at which the corrosion inhibitor concentration \( (Ce^{+3}) \) of the electrolyte (inside the scratch) lies between 10\(^{-3} \) M and 10\(^{-4} \) M. The error-bars show the standard deviation on the sample-set of 90 different slices. Furthermore, the particle circumradius compared to the unit sphere \( (R_c) \) denoted inside each bar.

![Figure 5.8: The effect of using uni-dimensional platonic, archimedean and spherical solids on the concentration of released corrosion inhibitor of scratches of different widths \( (f(dx)) \). Each bar in the graph represents the allowed scratch size at which the corrosion inhibitor concentration \( (Ce^{+3}) \) of the electrolyte (inside the scratch) lies between 10\(^{-3} \) M and 10\(^{-4} \) M. The error-bars show the standard deviation on the sample-set of 90 different slices. The particle circumradius compared to the unit sphere \( (R_c) \) denoted inside each bar.](image)

First of all, figure 5.8 shows a protected scratch size \( (dx) \) that is several orders in magnitude larger than expected. Experimental work [25, 116] and modeling work [115] show that only small damages (maximum scratch size of 2.5 mm) can be protected by inhibitor containing coatings. A back-of-the-envelope calculation has been used to confirm that no mistakes where made during the process and can be found in Appendix N. Based on this, there were six important reasons thought of why our model shows protection for larger damages:

1. The model does not take release kinetics into account (e.g. inhibitor throwing power [10], diffusion models [66, 68] and controlled release [21, 22]) which have a significant effect on the actual...
Chapter 5. *Effect of carrier geometry & size on the corrosion inhibitor release: a modeling approach*

1. The concentration of released corrosion inhibitor. This is most probably the main reason for the big difference.

2. It was assumed that the electrolyte fills up the complete volume of the scratch. Figure 5.9 shows how this assumption is unrealistic for small and large scratch sizes.

![Figure 5.9](image)

*Figure 5.9: Realistic electrolyte exposures at the scratch for (a) small and (c) large scratches compared to the modeled electrolyte (b).*

It can be seen that for small scratches (a) most of the electrolyte will be available on top of the coating (e.g. as a droplet as shown in figure), thereby decreasing the concentrations compared to the assumed volume (b). On the other hand, for larger scratches (c) it is not likely that the complete area of the scratch is exposed to electrolyte due to surface tension.

3. Most experimental tests are done with large volumes of electrolyte (e.g. standard electrochemical cells).

4. Currently only nanoparticles have been used and tested as corrosion inhibitor carrier while microparticles are used in our results.

5. The thickness of 100 µm is a relatively thick coating

6. The release of corrosion inhibitor is only roughly estimated and based on the carriers without taking the possible interactions of the coating into account.

The above-mentioned limitations of our model results in a scratch size that might not be realistic. To proof this, experimental validation tests under similar conditions and the introduction of kinetic models (as is done in the work of Javierre et al. [66]) are required. At this moment, the results of the model can and will only be used to compare the effect of changing the carrier shape on the release concentration of corrosion inhibitors, without making any statements on the protected scratch size.

When the different shapes are compared to each other it can be seen that the geometry of the particle has a significant effect on the released amount of $Ce^{3+}$. It can be seen that the increase of the particle circumradius (R) is in line with the released amount of $Ce^{3+}$. Figure 5.10 illustrates the meaning of the circumradius in 2D for a circle, cube and triangle which all have the same area.

![Figure 5.10](image)

*Figure 5.10: Illustration of the circumradius for a square ($r_s$) and triangle ($r_t$) with the same area as the unit circle ($r_c$).*

The same principle also holds for 3D shapes. The smallest circumradius is obviously for the sphere, which also results in least amount of release of corrosion inhibitors. This is interesting because the
Chapter 5. Effect of carrier geometry & size on the corrosion inhibitor release: a modeling approach

spherical shapes are often used as carrier geometry in self-healing coatings [76]. The release concentrations increases when the geometry circumradius increases, while the volume of corrosion inhibitor per particle is kept the same. This is true for both the platonic as archimedean solids. The highest release concentration is reached by the tetrahedron (R=2) resulting in an increase of 45% in release concentration. Thus, by increasing the circumradius of the geometry, the chance that a particle is dissected in the 2D plane increases significantly. If this assumption is true, multi-dimensional shapes with high aspect ratios should result in even larger circumradi, thereby higher release concentrations.

5.4.1.2 Multi-dimensional dependent shapes

Figure 5.8 shows the effect of using multi-dimensional solids on the concentration of released corrosion inhibitor of scratches of different widths \((f(dx))\). Each bar in the graph represents the allowed scratch size at which the corrosion inhibitor concentration \((\text{Ce}^{+3})\) of the electrolyte (inside the scratch) lies between \(10^{-3} M\) and \(10^{-4} M\). The error-bars show the standard deviation on the sample-set of 90 different slices. Furthermore, the particle circumradius compared to the unit sphere \((R)\) is denoted inside each bar.

![Figure 5.11: Effect of using multi-dimensional solids on the concentration of released corrosion inhibitor of scratches of different widths \((f(dx))\). Each bar in the graph represents the allowed scratch size at which the corrosion inhibitor concentration \((\text{Ce}^{+3})\) of the electrolyte (inside the scratch) lies between \(10^{-3} M\) and \(10^{-4} M\). The error-bars show the standard deviation on the sample-set of 90 different slices. The particle circumradius compared to the unit sphere \((R)\) is denoted inside each bar.](image)

The results shown in figure 5.11 confirm that the circumradius of the shape is directly related to the release concentration of corrosion inhibitor for our model. These results also agree with the numerical study performed by Mookhoek et al. [65] that higher aspect ratio of elongated capsules have a positive influence on the calculated release of liquid healing agents per crack area.

When cylindrical and cuboid shapes are compared at similar aspect ratios (assigned with an A in figure 5.11), it can be seen that rods and bars result in higher circumradius and release concentrations than the disk and sheetlike particles. Furthermore, the circumradius of sheets will increase more rapidly compared to disks due the fact that disk better represent the circular geometries. This means that larger aspect ratios for disks are required to reach the same release as for sheets.

Figure 5.12 shows the effect of using different cuboid shapes with aspect ratios \([01:x:12]\) where \(x=1,2,..12\) on the release at the damaged site width \((f(dx))\). They are shown in order of increasing scratch size (allowed concentrations).
It can be seen in figure 5.12 that the relation between increasing aspect ratio for increasing release does not apply in some cases, e.g. the [01:12:12] cuboid has a smaller circumradius than the [01:03:12]. However, the [01:12:12] reaches higher release concentrations. It must be that a flat sheet has a bigger chance of being dissected compared to a more rod-like particle that fits inside the same circumradius. The [01:01:12] rod leads to the highest release concentration, showing a 130% increase compared to spheres (see figure 5.8).

In conclusion, the results show that the modeling study does not agree with the width of the used scratch sizes found in literature, indicating that there are important factors (e.g. release kinetics, carrier size and representative experimental conditions) that have to be taken into account for further validation. However, the model does show that the amount of available corrosion inhibitor is influenced by the particle shape. The release can be significantly increased by particles with the same volume but with a larger circumradius (e.g. aspect ratio) combined with effectively using this space. This proofs that changing the particle shape can be used to optimize the released amount corrosion inhibitor without changing the PVC or total volume of the particles, whereby multi-dimensional dependent shapes (e.g. cylinders and plates) show the most potential.
5.4.2 Effect of carrier size on the corrosion inhibitor release concentration

The effect of the particle size on the corrosion inhibitor release concentration is evaluated by modeling a box filled with particles. The boundary conditions (i.e. box size, wall conditions and PVC) are explained in section 5.2.1. Spherical particles are used as example in this discussion because they require the least processing time and they can be used to relate the particle radius to the results. However, other shapes could have been used as well. Each individual model contains particles with the same size. The model is repeated 10 times for a particular particle size. This model is dissected 9 times in the xy-plane, resulting in 90 slices of 500 $\mu m$ by 100 $\mu m$ per particle shape. The average number of particles ($N_P$) per area ($mm^2$) is calculated for each slice as explained in section 5.3.1. This process is repeated for different particle sizes, which are shown in table 5.1.

<table>
<thead>
<tr>
<th>Particle radius ($\mu m$)</th>
<th>Particle volume ($\mu m^3$)</th>
<th>Particles per $mm^3$</th>
<th>PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>3.00E+01</td>
<td>1.00E+07</td>
<td>30%</td>
</tr>
<tr>
<td>4.2</td>
<td>3.00E+02</td>
<td>1.00E+06</td>
<td>30%</td>
</tr>
<tr>
<td>6.2</td>
<td>1.00E+03</td>
<td>3.00E+05</td>
<td>30%</td>
</tr>
<tr>
<td>11</td>
<td>6.00E+03</td>
<td>5.00E+04</td>
<td>30%</td>
</tr>
<tr>
<td>19</td>
<td>3.00E+04</td>
<td>1.00E+04</td>
<td>30%</td>
</tr>
</tbody>
</table>

These results are used to calculate the scratch size ($dx$) through equation 5.4 as discussed in section 5.3.2.

For infinite systems (i.e. large number of particles) the effect of changing the particle size can easily be calculated. The calculations in Appendix O show that the particle size is scalable under infinite conditions. The results from the model with the largest amount of particles (smallest particles) is the closest to an infinite system and can be used to calculate the expected effect for increasing the particle size for infinite systems.

Figure 5.13 shows the effect of changing the size of spherical particles in the coating on the concentration of released corrosion inhibitor of scratches of different widths ($f(dx)$). The different particle sizes used for the model are shown in table 5.1. The unfilled area represents the allowed scratch size at which the corrosion inhibitor concentration ($Ce^{+3}$) of the electrolyte (inside the scratch) lies between $10^{-3}M$ and $10^{-4}M$ and is based on the modeled results. The red line shows the expected outcome when scalability is assumed and the error-bars show the standard deviation on the sample-set of 90 different slices.
Chapter 5. Effect of carrier geometry & size on the corrosion inhibitor release: a modeling approach

**Figure 5.13:** The simulated effect of changing the size of spherical particles in the coating on the concentration of released corrosion inhibitor of scratches of different widths ($f(dx)$). Each bar in the graph represents the allowed scratch size at which the corrosion inhibitor concentration ($Ce^{+3}$) of the electrolyte (inside the scratch) lies between $10^{-3} M$ and $10^{-4} M$. The error-bars show the standard deviation on the sample-set of 90 different slices.

From figure 5.13 it can be seen that increasing the particle size also results in higher release of corrosion inhibitor. This result indicates that is better to use microparticles instead of nanoparticles to increase the inhibitor release. However, it has to be taken into account that the particle distance will also increase when large particles are used. This can result in zero-release for damage sizes which are in the same order of magnitude as the particle distance.

It can also be seen from figure 5.13 that for increasing particles size ($radius > 5 \mu m$), the model starts to diverge from the expected results when scalability is assumed. This is because the modeled coating systems are not completely scalable (e.g. coating thickness is fixed). In the case for the largest particle, the size of the particle is only 2.6 times smaller than the coating thickness and will results in different packing behavior compared to infinite systems. Furthermore, periodic wall conditions were used, as discussed in section 5.2.1. At a later stage in the process, it was found out that our mathematical representation for coating systems treated the model as a semi-infinite system (particles partly outside the box are calculated as if they are completely inside), resulting in an incorrect increase of $dx$ for larger particles.

In order to correct this mistake, the simulations were repeated but now under solid boundary conditions instead of periodic wall conditions. Figure 5.14 shows the effect of changing the wall boundary conditions from periodic to solid for the results shown in figure 5.13.
Chapter 5. Effect of carrier geometry & size on the corrosion inhibitor release: a modeling approach

Figure 5.14: The effect of changing the wall boundary conditions from periodic to solid for the results shown in figure 5.13. Trendline indicates relation that increase in particle equals the increase in $dx$.

In figure 5.14 it can be seen that changing the wall boundary conditions from periodic to solid results in a better representation of the expected value as if the model would be completely scalable. This is because the particles are now always completely inside the boundaries of the box (independent of their size), which fits better to our mathematical model. However, it also results in a depletion zone at the boundary which is not realistic when only a small section of the coating ($500 \times 100 \, \mu m$) is used. The effect of changing the boundary conditions on the outcome have to be better understood (e.g. experimentally) to make further suggestions on the conditions that results in the most realistic outcome. Furthermore, an increase in standard deviation for larger particles (different result for each individual slice) can be observed for both wall conditions. This is most likely related to the difference in the number of dissected particles per slice versus the particle volume.

Despite the current limitations of the model, the trend that increasing particle size also results in higher release of corrosion inhibitor is clearly visible. However, large particles will also result in over-protection for small damages. Figure 5.15 illustrates the of effect of particle size and release type on the corrosion protection for small and large damages.

Figure 5.15: Effect of particle size and release type on the corrosion protection.

From figure 5.15 is can be seen that small particles will never release sufficient amount of corrosion inhibitor at large damages. On the other hand, large particles will not be capable of protecting small damages unless a mechanism for controlled release is applied to prevent over-protection. However, even with controlled release there is the possibility that there are no particles exposed at the smaller damages. This means that the best corrosion protection system has to be a smart combination of differently sized particles combined with the implementation of controlled release systems.
5.5 Conclusion

In this chapter a particle packing model is successfully used to study the influence of carrier geometry and shape on the concentration of released corrosion inhibitor at scratches of different widths. Two particle packing codes are introduced. The first code works through a static triangulation algorithm combined with a trial-and-error approach. The second pre-developed code works through event-driven molecular dynamics combined with Monte Carlo displacement algorithms. The second code showed the most potential for our work and is used to represent our modeled coating with variable particle shapes and sizes. The damage at the coating is described mathematically whereby the number of exposed particles is acquired from the model.

It is shown that our modeling approach results in scratch widths which do not agree with literature, indicating that there are important factors (e.g. release kinetics, carrier size and experimental conditions) that are different and have to be taken into account for further comparison. Despite this, the results do show that the concentration of released corrosion inhibitor is influenced by the particle shape. The release is significantly increased by particles with a larger circumradius (e.g. high aspect ratios) combined with effectively using this space without changing the particle volume. This proofs that the particle shape has an effect on the concentration of released corrosion inhibitor at damages and can be used for optimization without changing the PVC or volume of the particles.

Finally it is shown the amount of released corrosion inhibitor is increased for bigger particles and that the best corrosion protection system has to be a smart combination of differently sized particles combined with the implementation of controlled release systems to prevent over-protection.

5.6 Recommendations

The work in this chapter is a good illustration of the current possibilities of using particle packing algorithms for carrier containing coatings. However, validation of the model by experimental work has not yet been achieved although it is extremely important to gain accurate and credible results. The first stage validation would be to compare the 3D packing models with x-ray tomography measurements on coatings with known properties (e.g. PVC, particle size and shape). The second stage validation would be the comparison between the mathematical representation of the scratched coating by electrochemical experiments. The current results have already shown that a couple of important improvements have to be made before this comparison can be achieved. The experimental conditions (e.g. amount of electrolyte, scratch width and surface topology) need to be examined with more detail and the mathematical representation has to be improved (e.g. including release kinetics and more accurate calculations on the exposed volume of particles). Additionally, a better representation of large particles could maybe be realized by keeping the number of particles constant and change the box size instead of keeping the box-size constant.

After the validation it would be interesting to use the model for the optimization of corrosion protection. In more detail, use the parameters of the coating (e.g. thickness, type of corrosion inhibitor and substrate) to calculate the best combination of carrier sizes and shapes to reduce the amount of particles and corrosion inhibitor in the coating.

The work shown in this chapter can also be used as starting point for models on other particle containing systems (e.g. extrinsic self-healing, phase-change and thermal-interface materials) which could result in new and interesting knowledge.
Conclusion

In this work a feasibility study of diatom frustules for corrosion inhibitor release in self-healing protective coatings has been performed. The frustules of the main centric type of diatom species *Aulacoseira* were obtained from one type of diatomaceous earth (DiaFil 525) through a water separation process followed by chemical treatments (i.e. acid and/or alkaline). For the doping, several different loading methods were explored (i.e. by dispersion at 23 and 60°C, in saturated inhibitor solution, and by capillarity) to introduce a model corrosion inhibitor (*Ce(NO₃)₃*) known for its inhibition efficiency of aerospace aluminium alloy AA2024-T3 corrosion. It was found that best controllable and highest loading method was achieved by evaporating the saturated corrosion inhibitor solution resulting in precipitation of *Ce(NO₃)₃* onto the inner and outer surface of the frustules. The versatility of the doping method was shown by successfully using other corrosion inhibitors (i.e. LiCl, Na-DEDTC and Na-2-MBT) as well. However, differences in the final doped diatom frustules were found depending on the inhibitor (e.g. deposition mainly outside the frustules). Despite the success of this doping method for the proof of concept it results clearly show that modifications or alternatives of the doping procedure should be developed in order to control and increase the amount of inhibitor contained in the diatom frustules. As an explorative route to improve the doping procedure the inclusion of zeolite structures in the diatoms was suggested. The concept was preliminary explored in this work by the co-deposition of pre-synthesized zeolites with the corrosion inhibitor. Such an approach should lead in the future to a better understanding of distinctive release kinetics by different release triggers. This could open the doors for in-situ zeolite growth in the frustules allowing for a combination of ion-exchange from the inhibitors in the zeolites and diffusion control release form the inhibitors deposited in the inner frustule volume.

In order to evaluate the doping degree and release kinetics from diatom frustules a new in-situ detection system was developed and validated. The concept combines in situ measurements of inhibitive species during release by UV spectroscopy. Such an approach allows accurately obtaining the fast release kinetics from carriers in a much more efficient and reliable manner. The first results show that the release rate of the of *Ce(NO₃)₃* corrosion inhibitor from frustules is different than its own fast dissolution rate, thereby suggesting that the release kinetics of corrosion inhibitor can be altered by the frustule carrier properties. Based on this work, the incorporation of a micro-capillary device combined with multiple in-situ measurement techniques is recommended to gain more fundamental knowledge on single carrier particles for the doping, release and corrosion protection. Furthermore, the relatively small differences in release kinetics with and without frustules pointed at the need of using inhibitors with lower dissolution rates possibly highlighting more the effect of the carrier, as well as incorporating on-demand release concepts to the frustules (e.g. pH triggered nanogates).

The protective behavior of the doped diatom frustules was then evaluated using *Ce(NO₃)₃* containing diatom-doped particles in an epoxy coating on top of an AA2024-T3 substrate. For a better analysis an in-situ opto-electrochemical technique previously developed for corrosion inhibitor behavior analysis was improved and implemented to analyze (damaged) coatings. Such a technique allowed a more accurate analysis and differentiation of the electrochemical signal responses related to corrosion processes.
Conclusion

and protection mechanisms. The results show that, without further optimization of the formulation or
the doping and release mechanism, protection of AA-2024-T3 coated plates of up to 27 days immersion
in 0.05 M NaCl are possible when 30% pigment volume concentration is used in a 70 \( \mu \text{m} \) thick coating.
This work proved the advantages of using the opto-electrochemical technique which at the same time
can be further optimized to allow quantification of processes such as delamination, underfilm pitting and
blistering as well as facilitating the correlation between the electrochemical signal and the degradation
process itself. The high efficiency of the inhibiting system was also proven demonstrating thereby the
high potential of the concept of corrosion control using diatom frustules.
As mentioned in the project, the proof of concept was developed using a given diatom, not a selected
one, despite the high aspect ratio geometry suggested its appropriateness. It was then questioned if
the geometry used would be the best possible one (obviating the presence of nanopores). In order to
advise on the best possible carrier geometry for active corrosion protection and establish the first steps
to the theoretical limits of the concept, a modeling approach was followed. The model showed that the
corrosion inhibitor release at a damage can be tuned by the carrier size and further optimized by using
shapes with a high aspect ratio. A combination of the appropriate shape and multiple combined sizes of
the carriers with controlled release concepts and more efficient inhibitors than those used in this work
may allow for a long-term efficient protection of small and large damages.

Based on the research done and the extracted conclusions this work shows that diatom frustules repre-
sent a very promising new natural carrier for corrosion inhibitors with potential of offering long term
protection of relatively big damages. This work sets up the basis for future research in the use of the big
diatom family with more than 10,000 different architectures as carriers for controlled release in coatings
as well as other functional agents for multifunctional applications in engineering applications.
## Appendix A

### Technical datasheet - DiaFil 525

**PRODUCT**

<table>
<thead>
<tr>
<th>Type</th>
<th>Functional Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>Natural Diatomite</td>
</tr>
</tbody>
</table>

**TYPICAL PHYSICAL PROPERTIES**

<table>
<thead>
<tr>
<th>Colour</th>
<th>White</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Fine powder</td>
</tr>
<tr>
<td>Hegman Index</td>
<td>1.5</td>
</tr>
<tr>
<td>Loose weight, lbs./cu. ft. (g/cc)</td>
<td>13.0 (0.21)</td>
</tr>
<tr>
<td>140 Mesh screen analysis, % retain</td>
<td>0.1</td>
</tr>
<tr>
<td>325 Mesh screen analysis, % retain</td>
<td>1.0</td>
</tr>
<tr>
<td>Oil absorption (% by weight)</td>
<td>120</td>
</tr>
<tr>
<td>Water absorption (% by weight)</td>
<td>160</td>
</tr>
<tr>
<td>Median particle size, microns</td>
<td>12.0</td>
</tr>
<tr>
<td>pH (10% in water)</td>
<td>8.0</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.3</td>
</tr>
<tr>
<td>Moisture (% by weight as shipped)</td>
<td>3.0</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.43</td>
</tr>
</tbody>
</table>

**TYPICAL CHEMICAL PROPERTIES (% by weight)**

| SiO₂   | 89.0 |
| Al₂O₃  | 4.0  |
| Fe₂O₃  | 1.7  |
| P₂O₅   | 0.2  |
| CaO    | 1.4  |
| MgO    | 0.6  |
| Na₂O + K₂O | 1.7 |
| Crystalline silica | < 0.1 |

*Typical values are not to be used as specifications*

The physical or chemical properties of Cellite products represent typical, average values obtained in accordance with generally accepted test methods and are subject to normal manufacturing variations. They are supplied as a technical service and are subject to change without notice. Technical data shown above are considered accurate and reliable, however, no guarantee is given or intended. For important Health & Safety information, please refer to MSDS.
Appendix B

Particle Size Distribution Diagram for Diafil 525

Figure B.1: Particle Size Distribution for Diagram for Diafil 525
Appendix C

SEM-EDX results for diatom frustules loaded methods with $Ce(NO_3)_3$

C.1 Loading by dispersion at 23°C

Figure C.1: SEM-EDX spectra for diatom frustules with $Ce(NO_3)_3$ using different frustule obtention treatments for loading by dispersion at 23°C.
Appendix C. SEM-EDX results for diatom frustules loaded methods with $\text{Ce(NO}_3\text{)}_3$

C.2 Loading by dispersion at 60°C

Figure C.2: SEM-EDX spectra for diatom frustules with $\text{Ce(NO}_3\text{)}_3$ using different frustule obtention treatments for loading by dispersion at 60°C.
C.3 Loading by capillarity

Figure C.3: SEM-EDX spectra for diatom frustules with $\text{Ce(NO}_3\text{)}_3$ using different frustule obtention treatments for loading by capillarity.
Appendix C. SEM-EDX results for diatom frustules loaded methods with $\text{Ce(NO}_3\text{)}_3$

C.4 Loading in saturation

Figure C.4: SEM-EDX spectra for diatom frustules with $\text{Ce(NO}_3\text{)}_3$ using different frustule obtention treatments for loading in saturation.
Appendix D

XRD analysis

Samples
The four powder samples are labeled: "sample-1_Diafil-525", "sample-2_SD-H2O-Ce" and "sample-3_CeNO3"; sample-0106-DE+H2O+CeNO3 (Epoxy coating containing doped diatom frustules)

Specimens
A small amount of powder was fixed on a thin layer of vacuum grease on a Si510 wafer.

Experimental
Instrument: Bruker D8 Advance diffractometer Bragg-Brentano geometry and Lynxeye position sensitive detector. LL 0.19 W 0.06. Cu K radiation. Divergence slit V12 (for sample 4 V6), scatter screen height 5 mm, 45 kV 40 mA.

Measurement: Coupled -2 scan 5 - 130, step size 0.040 2, counting time per step 1 s (for sample 4 4s). Sample spinning.

Data evaluation: Bruker software Diffrac.EVA vs 4.0.

Results
Figures 1 - 4 show the measured XRD patterns in black, after background subtraction. The colored sticks give the peak positions and intensities of the possibly present crystalline phases, using the ICDD pdf4 database, see table 1. Sample-1 seems to be mostly amorphous or microcrystalline.

In figure 4 shows the measured XRD pattern in black, after background subtraction. The sample seems to be partly amorphous. In the crystalline peak pattern no Cerium compounds could be detected.
Appendix D. **XRD analysis**

### D.1 As received Diafil 525

![XRD Results Sample-1: As received Diafil 525](image)

**Figure D.1:** XRD Results Sample-1: As received Diafil 525
Appendix D. *XRD analysis*

D.2 Water separated diatom frustules loaded with $\text{Ce(NO}_3\text{)}_3$ by loading in saturation

*Figure D.2: XRD Results Sample-2: Water treated Diafil 525 loaded with Cerium Nitrate (Loading in saturation method)*
Appendix D. XRD analysis

D.3 Pure $Ce(NO_3)_3$

Figure D.3: XRD Results Sample-3: Pure Cerium Nitrate Hexahydrate salt
D.4 Epoxy coating with Water separated diatom frustules loaded with $\text{Ce(NO}_3\text{)}_3$ by loading in saturation

Figure D.4: XRD Results Sample-4: Cured epoxy with embedded Water treated Diafil 525 loaded with Cerium Nitrate (Loading in saturation method)
Appendix E

Effect of adding NaY zeolites

In this appendix the addition of zeolites during the $Ce(NO_3)_3$ loading process of diatom frustules is discussed. Successful studies [21, 117] have shown that zeolites can be used as nanocarriers for cerium containing systems that have controlled corrosion inhibitor release due to ion-exchangeable processes. Furthermore, other studies [118, 119] have shown that diatoms can be used as supports for zeolites and combine the advantage of ion-exchange together with the porous silica structures of diatoms.

The NaY zeolite (CBV100) with an unit cell size of 24.65 Å was supplied by Zeolyst International. It has a silica/alumina ($SiO_2/Al_2O_3$) ratio of 5/1 and contains 13 wt% sodium oxide ($Na_2O$). The loading in saturation method was used, only now NaY zeolites are added. In this process 500 mg of diatom frustules are mixed together with 500 mg of NaY zeolites and 686 mg $Ce(NO_3)_3$. After this, 2 ml of water is added as solvent and the solution is placed on the shaking table at 320RPM for 72 hours. The solution is transferred to a round aluminium container and placed in an oven at 80°C under ambient atmosphere for 24 hours.

Figure 2.9 shows SEM images of the diatom/zeolite mixture after the loading treatment.

![SEM images of the diatom/zeolite mixture after the loading treatment.](image)

**Figure E.1:** $Ce(NO_3)_3$ doped diatom frustules with added NaY zeolites.

In figure E.1(a) it can be seen that many zeolites form separate aggregates. However, figure E.1(b) shows that the zeolites are also present at the inside and on the surface of the diatoms.

figure E.2 shows the SEM-EDX spectrum for for NaY Zeolites + Diatom Frustules loaded with $CeNO_3)_3$.
Appendix E. Effect of adding NaY zeolites

Figure E.2: SEM-EDX spectrum for NaY Zeolites + Diatom Frustules loaded with Ce(NO$_3$)$_3$

Cerium was detected by SEM-EDX as can be seen in figure E.2, although the SEM images do not show this. This suggests that a large quantity of cerium has ion-exchanged with the Na of the zeolites. Figure E.3 shows the SEM-EDX mapping for NaY Zeolites + Diatom Frustules loaded with Ce(NO$_3$)$_3$.

Figure E.3: SEM-EDX mapping for NaY Zeolites + Diatom Frustules loaded with Ce(NO$_3$)$_3$

From figure E.3 it can be seen that the amount of Cerium is indeed higher at locations where zeolites are located. These findings underpin the potential use of combined zeolite/diatomite doped systems, where diatoms act as carriers for zeolites loaded with cerium through ion-exchange.
Appendix F

UV-VIS Spectroscopy

F.1 Spectrum for $Ce(NO_3)_3$

Solutions at different concentrations of cerium nitrate hexahydrate $Ce(NO_3)_3$ are prepared. The absorbance spectrum is created for each sample in the 200-350nm wavelength.

Figure F.1: UV/VIS absorbance spectrum for $Ce(NO_3)_3$ at three different concentrations
F.2 Linear calibration curve for $\text{Ce(NO}_3\text{)}_3$

![UV-VIS Calibration curve for Ce(NO$_3$)$_3$ at $\lambda = 252$ nm](image)

**Equation:** $y = a + bx$

**Weight:** No Weighting

<table>
<thead>
<tr>
<th>Equation</th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual Sum of Squares</td>
<td>0.00462</td>
<td></td>
</tr>
<tr>
<td>Pearson's r</td>
<td>0.99971</td>
<td></td>
</tr>
<tr>
<td>Adj. R-Square</td>
<td>0.99934</td>
<td></td>
</tr>
</tbody>
</table>

**Absorbance**

- Intercept: -0.01211
- Slope: 1.65587

**Figure F.2:** UV/VIS Calibration curve for $\text{Ce(NO}_3\text{)}_3$ at $\lambda = 252$ nm
Appendix G

Defining Pigment Volume Concentration

The pigment volume concentration (PVC\textsuperscript{1}) is used in coating systems that contain solid particles, which act as pigments or fillers. The PVC is the final volume percentage of uniformly distributed particles in the dry coating system. For solid non-porous particles the PVC is simply formulated with the following equation:

\[ PVC = \frac{V_P}{V_P + V_M} \cdot 100\% \quad (G.1) \]

Where:
\( V_P = \text{Total pigment volume in the coating (cm}^3) \)
\( V_M = \text{Total (non-volatile) matrix volume (cm}^3) \)

In order to know how much mass of pigments has to be added during mixing, the bulk densities of the pigment (\( \rho_P \)) and matrix (\( \rho_M \)) are required.

\[ \rho_P = \frac{m_P}{V_P}; \quad \rho_M = \frac{m_M}{V_M} \]

Diatoms are open-porous structures with large empty voids. This means that the bulk density (including particle volume, inter-particle void volume, and internal pore volume) for DE will be different than the specific gravity of the material, which is 2.3 \( g \cdot cm^{-3} \). Besides the bulk density that is unknown, the voids will be filled with the matrix material and this also needs to be taken into account in order to correctly calculate the PVC. This makes it quite complicated to know the precise PVC. Here we explain the process that is used to calculate the free volume for diatoms that will be filled by the matrix and how this is used to find the relation between the diatom PCV and the required wt% of DE during mixing. After this is established, the effect on doping DE with corrosion inhibitor on the PVC is evaluated.

G.1 Free volume inside the diatom via geometrical calculations

In chapter 2 the shape for our diatom frustules was assumed to be a hollow cylinder with an outer radius \( (R) \), inner radius \( (r) \) and height \( (h) \). The wall of the frustule also consists out of small circular pores. The volume of the diatom frustule \( (V_{DE}) \) can be defined by

\[ V_{DE} = \frac{2}{3} \pi (R^2 - r^2) h \quad (G.2) \]

which is simply the equation to calculate the volume of a hollow cylinder, where \( \frac{2}{3} \) represents the assumed \( \frac{1}{3} \) volume loss for the small pores, based on the pore area fraction as shown in figure 2.2.

\textsuperscript{1}The PVC is calculated by leaving the volatile components (like water and solvents) out.
Appendix G. Defining Pigment Volume Concentration

The free volume inside the diatom ($V_{Free}$) can be defined by the following equation:

$$V_{Free} = \pi r^2 h + \frac{1}{3} \pi (R^2 - r^2)h$$  \hspace{1cm} (G.3)

This is simply the equation to calculate the volume of a solid cylinder, where $\frac{1}{3} \pi (R^2 - r^2)h$ represents the volume of the small pores that is added to the free volume, based on the pore area fraction as shown in figure 2.2.

The equation to find the percentage of free volume can now be calculated by dividing equation G.3 for the free volume by the total volume (free volume + volume of the diatom from equation G.2).

$$DE_{Free\ volume\ %} = \frac{V_{Free}}{V_{Free} + V_{DE}} \cdot 100\% = \frac{1}{3} \frac{R^2 + 2r^2}{R^2} \cdot 100\%$$  \hspace{1cm} (G.4)

It is interesting to see that in equation G.4 only the radius and wall thickness are dependent on the free volume, and not the height of the diatoms.

The following dimensions are assumed based on the known mean particle size for DE of 12 µm and the fact that the diatoms are thin walled (< 1 µm):

$R = 6.0 \ \mu m$

$r \geq 5.0 \ \mu m$

Equation G.4 result in a free volume inside the diatom of 80 vol% or more.

G.2 Free volume inside the diatom via water absorption data

Another simple method than can be used to calculate the free volume is with the use of the water adsorption and specific gravity data for the DE. The technical datasheet for Diafil 525 from Profiltra indicates that 160 wt% of water can be absorbed by the diatoms and that they have a specific gravity ($\rho_{DE}$) of 2.3 g · cm$^{-3}$.

$$\rho_{DE} = 2.3 \ g \cdot cm^{-3}$$

$$\rho_{Water} = 1.0 \ g \cdot cm^{-3}$$

$$DE_{Absorption} = 1.6$$

1.0 grams of diatomaceous earth can absorb 1.6 grams of water. Together with the use of the density for water ($\rho_{Water}$) and the specific gravity for diatomaceous earth ($\rho_{DE}$) we can calculate that the volume for diatomaceous earth ($V_{DE}$) is $\frac{1}{2.3}$ cm$^3$ and that this volume contains 1.6 cm$^3$ water, which is the free volume ($V_{Free}$). The percentage of free volume volume can now be calculated with the use of G.5.

$$DE_{Free\ volume\ %} = \frac{V_{Free}}{V_{Free} + V_{DE}} \cdot 100\% = \frac{1.6}{\frac{1}{2.3} + 1.6} \cdot 100\% = 79\%$$  \hspace{1cm} (G.5)

This result is very close to the free volume percentage found trough the geometrical analysis. Based on these results the free volume for Diafil 525 diatomaceous earth is presumed to be approximately 80%, which will be used in further calculations.

G.3 PVC conversion to weight percentage of pure DE

The next step is to calculate the relationship between the weight percentage of pigments and its volume percentage. It is assumed that the complete inner volume of the pigments ($V_P$) is completely filled with
the matrix during mixing. For this reason the density of the pigment \( \rho_p \) will be a combination of the specific gravity for the diatomaceous earth \( \rho_{DE} \) and the density of the matrix \( \rho_M \):

\[
\rho_p = \frac{m_p}{V_p} = \frac{m_{DE} + m_M}{V_{DE} + V_M} \quad \text{(G.6)}
\]

If we assume the following densities for the diatomaceous earth and the matrix:

\[
\rho_{DE} = 2.3 \text{ g cm}^{-3} \Rightarrow m_{DE} = \rho_{DE} \cdot V_{DE} \\
\rho_M = 1.1 \text{ g cm}^{-3} \Rightarrow m_M = \rho_M \cdot V_M
\]

We can rewrite equation G.6

\[
\rho_p = \frac{\rho_{DE} \cdot V_{DE} + \rho_M \cdot V_M}{V_{DE} + V_M} \quad \text{(G.7)}
\]

Knowing that the matrix will fill 80% of the diatom volume \( V_M = 4V_{DE} \), we get the density of the pigment (diatomaceous earth filled with matrix):

\[
\rho_p = 1.34 \text{ g cm}^{-3}
\]

In this case all the pores of the diatomaceous earth are filled with matrix material. The weight of the matrix needs to be subtracted again in order to know how much weight of pure diatomaceous earth needs to be added during mixing to reach the required PVC. With use of the densities of the pigment and matrix, we can calculate the weight ratio between the matrix and the diatomaceous earth of the pigments:

\[
\frac{m_M}{m_{DE}} = \frac{\rho_M - 1}{1 - \frac{\rho_M}{\rho_{DE}}} = 0.52 \quad \text{(G.8)}
\]

Equation G.8 tells us that 34 wt% of the pigment is from the diatomaceous earth and the other 66 wt% by the matrix.

The relationship between the weight percentage concentration of diatomaceous earth \( DE_{wt\%} \) and the volume percentage concentration of pigments (PVC) can now easily be calculated. The density of the matrix and pigments is known and the weight percentage of diatomaceous earth in the pigment is calculated in equation G.8. If we rewrite this into equation G.1 we get:

\[
DE_{wt\%} = \frac{\rho_p^{\text{PVC}} \cdot 0.34}{(\rho_M - \rho_p)\left(\frac{\text{PVC}}{100} - \rho_M\right)} \cdot 100\% \quad \text{(G.9)}
\]

Equation G.9 shows that approximately 12 wt% diatomaceous earth is required to end up with a coating that contains 30% PVC. It is important to state again that in these calculations the free volume is estimated and that the presumption is made that all this volume is filled with the matrix, which in reality might not be the case. It is thereby recommended to always use a higher amount of diatomaceous earth in order to be sure that the required PVC is reached.

### G.4 Adding corrosion inhibitors to DE

At this point it is interesting to understand the effect on the PVC when a corrosion inhibitor is added to the system. To understand this relation we need to know the following things:

- The mass ration between undoped diatoms and inhibitor
- The density of the corrosion inhibitor \( \rho_I \)
- The location of the corrosion inhibitor.
Appendix G. Defining Pigment Volume Concentration

For our calculations it is assumed that all the corrosion inhibitor is present inside and outside the diatom, creating a thin layer around the diatom. For the next equations we have assumed the following parameters:

\textit{Cerium Nitrate Hexahydrate (Ce(NO\textsubscript{3})\textsubscript{3}) as corrosion inhibitor}

\( \rho_I = 1.67 \text{ g cm}^{-3} \)

\( m_{DE} = 1.5 \times m_I \)

First the bulk density for the diatom is calculated whereby the free volume is assumed empty (vacuum):

\[
\rho_{DE, \text{bulk}} = \frac{m_{DE, \text{free}}}{V_{DE, \text{free}}} = \frac{m_{DE}}{V_{DE} + V_{\text{free}}}
\]

And we know that \( V_{\text{free}} = 4V_{DE} \) and \( m_{DE} = 2.3V_{DE} \) These relations are combined with equation G.10 and gives the bulk density of the diatom where the inner area is empty:

\[
\rho_{DE, \text{bulk}} = 0.46 \text{ g cm}^{-3}
\]

We can now calculate the volume ratio between the diatom and inhibitor by combining above equation with the mass ratio between diatom and inhibitor trough their densities.

\[
\frac{V_I}{V_{DE, \text{Bulk}}} = \frac{\rho_{DE, \text{bulk}}}{\rho_I \cdot 1.5} = \frac{0.46}{1.67 \cdot 1.5} = 0.18
\]

This means that only 16% of the bulk volume would be filled with the corrosion inhibitor, which has a slightly higher density than the matrix that would have filled this volume. The percentage will even be lower if we take into account that not all the corrosion inhibitor is located inside the diatom. The difference in PVC between undoped and doped diatoms (in this case) will be small, because the density of the corrosion inhibitor is close to that for the matrix and it requires only a small part of free volume at this concentration. However, the calculations can change drastically if the corrosion inhibitor prevents the matrix to fill the free volume inside the diatoms. This will result in an higher percentage of diatomaceous earth to reach the same PVC.

The choice is made that the PVC increase of the corrosion inhibitor will be neglected during the mixing process, under the following conditions:

- The density of the corrosion inhibitor is not below \( 1.0 \text{ g cm}^{-3} \)
- The mass ration between undoped diatoms and inhibitor does not exceed 1.5
- The corrosion inhibitor does not prevent the matrix to fill the free volume of the diatoms.

This means that all coating systems (with and without corrosion inhibitors) will contain the same wt% of undoped diatoms, resulting in roughly the same PVC.
Appendix H

Opto-Electrochemical video results

H.1 Sample: E (Damaged)

External link: https://youtu.be/m2Twhhr5Iio

¹The video is only compatible with Adobe Reader-9/X and requires internet access outside the web browser. The external links can be used if the page remains empty.
Appendix H. *Opto-Electrochemical video results*

**H.2 Sample: 1.5Ce-ED (Intact)**

External link: [https://youtu.be/sqbt_IvQ8mA](https://youtu.be/sqbt_IvQ8mA)

---

2The video is only compatible with Adobe Reader-9/X and requires internet access outside the web browser. The external links can be used if the page remain empty.
Appendix H. *Opto-Electrochemical video results*

**H.3 Sample: Primer+1.5Ce-ED (Damaged)**

External link: [https://youtu.be/Ixl98bBOhhc](https://youtu.be/Ixl98bBOhhc)\(^3\)

---

\(^3\)The video is only compatible with Adobe Reader-9/X and requires internet access outside the web browser. The external links can be used if the page remain empty.
Appendix H.  *Opto-Electrochemical video results*

### H.4 Sample: 0.15Ce-ED(1) (Damaged)

External link: https://youtu.be/w4E-Aq6qHhA

---

*The video is only compatible with Adobe Reader-9/X and requires internet access outside the web browser. The external links can be used if the page remain empty.*
Appendix H. *Opto-Electrochemical video results*

H.5 Sample: 0.15Ce-ED(2) (Damaged)

External link: [https://youtu.be/YF17_GWim7s](https://youtu.be/YF17_GWim7s)\(^5\)

\(^5\)The video is only compatible with Adobe Reader-9/X and requires Internet access outside the web browser. The external links can be used if the page remains empty.
Appendix I

Packing algorithm of spheres through static triangulation techniques

```matlab
clear;
clc;

% Generate cube
L = 0.1 ; %input('Enter Sample Length (mm): ');
B = 0.1 ; %input('Enter Sample Width (mm): ');
H = 0.05 ; %input('Enter Sample height (mm): ');
CA = [0 0 0];
CB = [L 0 0];
CC = [0 B 0];
CD = [0 0 H];
CE = [0 B H];
CF = [L 0 H];
CG = [L B 0];
CH = [L B H];
P = [CA;CB;CF;CH;CG;CC;CA;CD;CE;CH;CF;CD;CE;CC;CG;CB];

%Volume of cube (m^3)
Vc = (L*B*H)*10^-9;

%Calculate volume of spherical diatom (m^3)
Dr = 4; %input('Enter mean diatom radius (microns): ');
Dr = Dr * 10^-3;
Dh = 10; %input('Enter diatom hieght (mm): ');
Vd = ((4/3)*pi*(Dr^3))*10^-9;

%Fill cube with x random points
X = 10 ;%input('Input amount of diatoms (volume percentage)');
Dvol = round((Vc*(X/100))/Vd);
DvolMax = round(Dvol*1.4);
Overlap01asum=0.1;
while Overlap01asum > Dr/100 % not more than one sphere overlap in order to complete
    r0 = rand(DvolMax,3);
    rL = r0(:,1)*L;
    rB = r0(:,2)*B;
    rH = r0(:,3)*H;
    V = [rL, rB, rH];

    % Construct their Delaunay triangulation: tetrahedral mesh
    T = delaunay(V(:,1),V(:,2),V(:,3));

    % Gather all edges of the tet mesh
    E = [ T(:,1) T(:,2); T(:,2) T(:,3); T(:,3) T(:,4); T(:,4) T(:,1)];

    % include both edge directions
    E = [E; fliplr(E)];

    % Indices of source vertex of each edge as seen by each other vertex
    EE1 = repmat(E(:,1),1,size(V,1));
```

92
Appendix I. Packing algorithm of spheres through static triangulation techniques

```matlab
% length of each edge
d = (sqrt(sum((V(E(:,1),:) - V(E(:,2),:)).^2,2)));% length as seen by each other vertex
DD = repmat(d,[1,1,size(V,1)]);% indices of all vertices as see by each edge (source vertex)
II = repmat(1:size(V,1),size(E,1),1);% create a mask that is infinity if source vertex == vertex
mask = (EE1 == II).^(-1);% compute minimum distance to any vertex: radius of largest sphere

r2 = normrnd(Dr,0.0005,[1,Dvol]);% Radius to reach required volume percentage of diatoms
r2Sort = sortrows(r2.',1).';

r4 = [1:1:DvolMax;min(mask.*DD)./2];%Delunay triangilation for all points
secondrowr4 = r4(:,2);
idx0 = secondrowr4 < r2Sort(:,1);
idx1 = secondrowr4 >= r2Sort(:,1);
r40 = r4(idx0,:);%Values of locations that are small
r40 = [r40(1,:);Empty1];%Values of locations that are large enough

r4 = [r40(1,:), r41(1,:), r40(2,:), r41(2,:)];% combine to have complete set again

rtotal = [rSort1(:,(DvolMax+1)-Dvol:DvolMax);r2Sort];
rtotalEmpty = [r_sort1(:,1:DvolMax-Dvol);zeros(1,size(r_totalEmpty,2))];
% Numbers that have to stay empty

% Try to make ellipses and not spheres
rtotalAll2 = [rtotalAll(2,:);rtotalAll(2,:);rtotalAll(2,:)];

rtotalAllCheck = [rtotalAll;rt1];
Overlap = sum(rtotalAllCheck(3,:)<rtotalAllCheck(2,:))
Overlap01 = (rtotalAllCheck(3,:)<rtotalAllCheck(2,:));%overlap of radius over all spheres
Overlap01a = Overlap01(1,:).*(rtotalAllCheck(3,:)-rtotalAllCheck(2,:));
Overlap01asum = abs(sum(Overlap01a))/Overlap%

end
% Check if it indeed is consistent with the asked volume percentage and %radius
%FinalVolumePercentage = (1/(Vc/sum(((4/3)*pi.*(rtotalAll(2,:).^3))*.10^-9))))*100
%FinalMeanRadius = sum(rtotalAll(2,:))/Dvol
%FinalStd = std(rtotalAll(2,:))

%plot mesh and balls
figure
subplot(1,3,1);
plot3(rL,rB,rH,'.'); axis equal
%campos([8,-4.5,5])
title('Random points');

subplot(1,3,2);
tetramesh(T,V,'FaceAlpha',0.1);
```

93
Appendix I. Packing algorithm of spheres through static triangulation techniques

axis equal
campos([8,-4.5,5])
title('Delaunay tessellation');

subplot(1,3,3);
bubbleplot3(V(:,1),V(:,2),V(:,3),rtotalAll2,repmat([0.3,0.2,0.7],size(V,1),1))
axis equal
campos([8,-4.5,5])
title('conservative packing of spheres');
shading interp; camlight right; lighting phong;
Appendix J

Geometrical formulas

J.1 Platonic solids

<table>
<thead>
<tr>
<th>Solid</th>
<th>Vertices</th>
<th>Edges</th>
<th>Faces</th>
<th>Volume</th>
<th>Surface Area</th>
<th>Circumradius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedron</td>
<td>4</td>
<td>6</td>
<td>4</td>
<td>$\frac{1}{\sqrt{2}}$ = 0.707107</td>
<td>$\sqrt{2}$ = 1.414214</td>
<td>$\sqrt{3}$ / 2 = 0.866025</td>
</tr>
<tr>
<td>Hexahedron</td>
<td>8</td>
<td>12</td>
<td>6</td>
<td>1</td>
<td>6</td>
<td>$\sqrt{2}$ / 2 = 0.707107</td>
</tr>
<tr>
<td>Octahedron</td>
<td>6</td>
<td>12</td>
<td>8</td>
<td>$\frac{\sqrt{2}}{3}$ = 0.471405</td>
<td>$2 \sqrt{3}$ = 3.46411</td>
<td>$\frac{1}{\sqrt{2}}$ = 0.707107</td>
</tr>
<tr>
<td>Dodecahedron</td>
<td>20</td>
<td>30</td>
<td>12</td>
<td>$\frac{1}{4} (5 + 7 \sqrt{5}) \approx 7.66312$</td>
<td>$3 (2 \sqrt{5} + 5 \sqrt{2}) \approx 20.6457$</td>
<td>$\frac{1}{4} (\sqrt{5} + 3 \sqrt{2}) \approx 1.6035$</td>
</tr>
<tr>
<td>Icosahedron</td>
<td>12</td>
<td>30</td>
<td>20</td>
<td>$\frac{5 \phi^2}{6} \approx 2.8069$</td>
<td>$5 \sqrt{3} = 8.66025$</td>
<td>$\frac{1}{4} (\sqrt{15} + 3 \sqrt{5}) \approx 0.951057$</td>
</tr>
</tbody>
</table>

Figure J.1: Geometrical formulas for platonic solids, assuming unit edge length distance.
## J.2 Archimedean solids

<table>
<thead>
<tr>
<th>Solid</th>
<th>Vertices</th>
<th>Edges</th>
<th>Faces</th>
<th>Volume</th>
<th>Surface Area</th>
<th>Circumradius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Truncated Tetrahedron</td>
<td>12</td>
<td>18</td>
<td>4</td>
<td>$\frac{23}{6\sqrt{2}} = 2.71658$</td>
<td>$7\sqrt{3} = 12.1244$</td>
<td>$\frac{12}{2} = 1.1726$</td>
</tr>
<tr>
<td>Cuboctahedron</td>
<td>12</td>
<td>24</td>
<td>14</td>
<td>$\frac{5\sqrt{2}}{3} = 2.35702$</td>
<td>$2(3 + \sqrt{3}) = 9.4641$</td>
<td>1</td>
</tr>
<tr>
<td>Truncated Cube</td>
<td>24</td>
<td>36</td>
<td>14</td>
<td>$\frac{7 + 14\sqrt{2}}{3} = 13.5997$</td>
<td>$2(6 + 6\sqrt{2} + \sqrt{3}) = 32.4347$</td>
<td>$\frac{1}{2} \sqrt{7 + 4\sqrt{2}} = 1.77802$</td>
</tr>
<tr>
<td>Truncated Octahedron</td>
<td>24</td>
<td>26</td>
<td>14</td>
<td>$\frac{8\sqrt{2}}{3} = 11.3137$</td>
<td>$6 + 12\sqrt{3} = 26.7840$</td>
<td>$\frac{6}{\sqrt{2}} = 1.58114$</td>
</tr>
<tr>
<td>Rhombicuboctahedron</td>
<td>24</td>
<td>48</td>
<td>26</td>
<td>$\frac{4 + 10\sqrt{2}}{3} = 8.71405$</td>
<td>$2(0 + \sqrt{2}) = 21.4041$</td>
<td>$\frac{1}{2} \sqrt{5 + 2\sqrt{2}} = 1.39907$</td>
</tr>
<tr>
<td>Truncated Cuboctahedron</td>
<td>48</td>
<td>72</td>
<td>26</td>
<td>$\frac{22 + 14\sqrt{2}}{3} = 41.799$</td>
<td>$12(2 + \sqrt{2} + \sqrt{3}) = 61.7552$</td>
<td>$\frac{1}{2} \sqrt{13 + 6\sqrt{2}} = 2.31701$</td>
</tr>
<tr>
<td>Snub cube</td>
<td>24</td>
<td>60</td>
<td>38</td>
<td>$\frac{10 \sqrt{3}}{3} = 19.8564$</td>
<td>$6 + 8\sqrt{3} = 19.8564$</td>
<td>$\frac{10 \sqrt{3}}{3} = 1.34071$</td>
</tr>
<tr>
<td>Icosidodecahedron</td>
<td>30</td>
<td>60</td>
<td>32</td>
<td>$\frac{1}{6} (45 + 17\sqrt{5}) = 13.6255$</td>
<td>$\sqrt{2}(11 + 5\sqrt{5} + 3\sqrt{13 + 6\sqrt{2}}) = 28.309$</td>
<td>$\frac{1}{2} (1 + \sqrt{5}) = 1.61803$</td>
</tr>
<tr>
<td>Truncated icosidodecahedron</td>
<td>60</td>
<td>90</td>
<td>32</td>
<td>$\frac{1}{12} (59 + 47\sqrt{5}) = 38.9397$</td>
<td>$\sqrt{2}(11 + 5\sqrt{5} + 3\sqrt{13 + 6\sqrt{2}}) = 51.8891$</td>
<td>$\frac{1}{4} (7 + 30\sqrt{5}) = 2.95945$</td>
</tr>
<tr>
<td>Icosahedron</td>
<td>60</td>
<td>90</td>
<td>32</td>
<td>$\frac{1}{12} (125 + 63\sqrt{5}) = 55.2877$</td>
<td>$\sqrt{2}(11 + 5\sqrt{5} + 3\sqrt{13 + 6\sqrt{2}}) = 72.0873$</td>
<td>$\frac{1}{4} (58 + 18\sqrt{5}) = 2.47902$</td>
</tr>
<tr>
<td>Rhombicosidodecahedron</td>
<td>60</td>
<td>120</td>
<td>62</td>
<td>$\frac{29 + 25\sqrt{5}}{3} = 41.8153$</td>
<td>$\sqrt{2}(11 + 5\sqrt{5} + 3\sqrt{13 + 6\sqrt{2}}) = 56.5641$</td>
<td>$\frac{1}{2} (11 + 4\sqrt{5}) = 2.22305$</td>
</tr>
<tr>
<td>Truncated icosicosahedron</td>
<td>120</td>
<td>180</td>
<td>62</td>
<td>$95 + 50 \sqrt{5} = 206.803$</td>
<td>$\sqrt{2}(11 + 5\sqrt{5} + 3\sqrt{13 + 6\sqrt{2}}) = 78.0595$</td>
<td>$\frac{1}{2} (21 + 12\sqrt{5}) = 3.80239$</td>
</tr>
<tr>
<td>Snub Dodecahedron</td>
<td>60</td>
<td>150</td>
<td>92</td>
<td>$\frac{105}{4\sqrt{5}} = 55.2877$</td>
<td>$\sqrt{2}(11 + 5\sqrt{5} + 3\sqrt{13 + 6\sqrt{2}}) = 65.2451$</td>
<td>$\frac{105}{4\sqrt{5}} = 3.80239$</td>
</tr>
</tbody>
</table>

**Figure J.2:** Geometrical formulas for archimedean solids, assuming unit edge length distance
Appendix K

Shell script for the modeling process

```bash
#!/bin/bash
for d in */ ; do
    echo "Begin processing $d"
    rm $d/*.png
    echo "All images in main-directory are deleted"
    mkdir $d/Run01_2D_Slices
    echo "Created subdirectory /Run01_2D_Slices"
    rm $d/Run01_2D_Slices/*.png
    mkdir $d/Run01_ImageJ_Particle_count
    echo "Created subdirectory /Run01_ImageJ_Particle_count"
    pack -o $d/output_01.pack $d/DiafilModel
    echo "Rocpack finished running first batch"
    echo "Start slicing $d/Run01_2D_Slices/"
    pack2mesh -v -q -l 5120 --slice z=0.1 $d/output_01.pack $d/Run01_2D_Slices/01_10.png
    echo "01_10.png"
    pack2mesh -v -q -l 5120 --slice z=0.2 $d/output_01.pack $d/Run01_2D_Slices/01_20.png
    echo "01_20.png"
    pack2mesh -v -q -l 5120 --slice z=0.3 $d/output_01.pack $d/Run01_2D_Slices/01_30.png
    echo "01_30.png"
    pack2mesh -v -q -l 5120 --slice z=0.4 $d/output_01.pack $d/Run01_2D_Slices/01_40.png
    echo "01_40.png"
    pack2mesh -v -q -l 5120 --slice z=0.5 $d/output_01.pack $d/Run01_2D_Slices/01_50.png
    echo "01_50.png"
    pack2mesh -v -q -l 5120 --slice z=0.6 $d/output_01.pack $d/Run01_2D_Slices/01_60.png
    echo "01_60.png"
    pack2mesh -v -q -l 5120 --slice z=0.7 $d/output_01.pack $d/Run01_2D_Slices/01_70.png
    echo "01_70.png"
    pack2mesh -v -q -l 5120 --slice z=0.8 $d/output_01.pack $d/Run01_2D_Slices/01_80.png
    echo "01_80.png"
    pack2mesh -v -q -l 5120 --slice z=0.9 $d/output_01.pack $d/Run01_2D_Slices/01_90.png
    echo "01_90.png"
    echo "end processing $d"
done;
```
Appendix L

ImageJ processing script

```java
1 dir1 = getDirectory("2D_Slices");
2 format = getFormat();
3 dir2 = getDirectory("ImageJ_Particle_count");
4 list = getFileList(dir1);
5 setBatchMode(true);
6 for (i=0; i<list.length; i++) {
7    showProgress(i+1, list.length);
8    open(dir1+list[i]);
9       run("8-bit");
10       setOption("BlackBackground", false);
11       run("Convert to Mask");
12       run("Set Scale...", "distance=1024 known=0.1 unit=mm");
13       run("Fill Holes");
14       run("Analyze Particles...", "size=0.0000001-Infinity");
15       if (format=="8-bit TIFF" || format=="GIF")
16          convertTo8Bit();
17       saveAs(format, dir2+list[i]);
18    close();
19 }
20 function getFormat() {
21     formats = newArray("TIFF", "8-bit TIFF", "JPEG", "GIF", "PNG",
22      "PGM", "BMP", "FITS", "Text Image", "ZIP", "Raw");
23     Dialog.create("Batch Convert");
24     Dialog.addChoice("Convert to: ", formats, "TIFF");
25     Dialog.show();
26     return Dialog.getChoice();
27 }
28 function convertTo8Bit() {
29     if (bitDepth==24)
30        run("8-bit Color", "number=256");
31     else
32        run("8-bit");
33 }
```

98
## Appendix M

### Particle packing results

<table>
<thead>
<tr>
<th>Category-1</th>
<th>Shape</th>
<th>Volume [mm$^3$]</th>
<th>Avg. Pigment Area Concentration [%]</th>
<th>Avg. Number of particles</th>
<th>Standard Deviation</th>
<th>WIN Number of particles</th>
<th>MAX Number of particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Other</td>
<td></td>
<td>0.00 x 0.00</td>
<td>0.00 x 0.00</td>
<td>0.00 x 0.00</td>
<td>0.00 x 0.00</td>
<td>0.00 x 0.00</td>
<td>0.00 x 0.00</td>
</tr>
</tbody>
</table>

---

### Notes:
- All values are provided in the document. Additional details or calculations are not included.
Appendix M. Particle packing results

| Disk | Cylinder (35-125) | 1.00E-06 | 30 | 351 | 12 | 125 | 178 |
| Disk | Cylinder (16-105) | 1.00E-06 | 30 | 362 | 13 | 351 | 427 |
| Disk | Cylinder (20-105) | 1.00E-06 | 30 | 407 | 18 | 386 | 455 |
| Disk | Cylinder (24-105) | 1.00E-06 | 30 | 426 | 21 | 371 | 477 |
| Platonic Solids | icosahedron | 1.00E-06 | 30 | 232 | 6 | 208 | 248 |
| Other | cube | 1.00E-06 | 30 | 232 | 6 | 212 | 252 |
| Platonic Solids | icosahedron | 1.00E-06 | 30 | 232 | 5 | 208 | 248 |
| Other | sphere | 1.00E-06 | 30 | 232 | 6 | 212 | 252 |
| Platonic Solids | icosahedron | 1.00E-06 | 30 | 232 | 5 | 208 | 248 |
| Other | prism | 1.00E-06 | 30 | 303 | 3 | 282 | 324 |
| Other | prism | 1.00E-06 | 30 | 246 | 3 | 216 | 266 |
| Other | prism | 1.00E-06 | 30 | 252 | 3 | 221 | 271 |
| Other | pyramid | 1.00E-06 | 30 | 281 | 3 | 251 | 301 |
| Other | pyramid | 1.00E-06 | 30 | 272 | 3 | 248 | 298 |
| Other | pyramid | 1.00E-06 | 30 | 269 | 3 | 252 | 298 |
| Other | reflected_squa_cube | 1.00E-06 | 30 | 251 | 3 | 234 | 289 |
| Other | reflected_squa_cube | 1.00E-06 | 30 | 212 | 3 | 194 | 232 |
| Archimedean Solids | parallelepipedoctahedron | 1.00E-06 | 30 | 212 | 7 | 195 | 239 |
| Archimedean Solids | parallelepipedoctahedron | 1.00E-06 | 30 | 227 | 7 | 210 | 254 |
| Other | cyndeltube | 1.00E-06 | 30 | 211 | 8 | 194 | 232 |
| Archimedean Solids | snub_cube | 1.00E-06 | 30 | 216 | 8 | 194 | 232 |
| Archimedean Solids | snub_dodecahedron | 1.00E-06 | 30 | 211 | 8 | 194 | 232 |
| Other | snub_trunc | 1.00E-06 | 30 | 230 | 7 | 207 | 254 |
| Spheres | sphere_1000 | 3.00E-07 | 30 | 412 | 3 | 370 | 437 |
| Spheres | sphere_10000 | 3.00E-07 | 30 | 443 | 3 | 416 | 474 |
| Spheres | sphere_100000 | 3.00E-07 | 30 | 26 | 7 | 23 | 27 |
| Spheres | sphere_1000000 | 3.00E-07 | 30 | 1868 | 29 | 1384 | 1962 |
| Spheres | sphere_10000000 | 3.00E-08 | 30 | 1584 | 25 | 1182 | 1997 |
| Spheres | sphere_100000000 | 3.00E-09 | 30 | 208 | 12 | 168 | 221 |
| Spheres | sphere_1000000000 | 3.00E-10 | 30 | 496 | 7 | 436 | 517 |
| Spheres | sphere_10000000000 | 3.00E-11 | 30 | 496 | 6 | 436 | 517 |
| Other | square_nel | 1.00E-06 | 30 | 463 | 13 | 416 | 474 |
| Platonic Solids | tetrahedron | 1.00E-06 | 30 | 353 | 9 | 285 | 357 |
| Archimedean Solids | trapezohedron | 1.00E-06 | 30 | 210 | 8 | 200 | 247 |
| Archimedean Solids | trapezohedron | 1.00E-06 | 30 | 212 | 8 | 195 | 239 |
| Archimedean Solids | trapezohedron | 1.00E-06 | 30 | 217 | 8 | 202 | 250 |
| Archimedean Solids | trapezohedron | 1.00E-06 | 30 | 211 | 8 | 194 | 232 |
| Archimedean Solids | trapezohedron | 1.00E-06 | 30 | 222 | 7 | 194 | 232 |
| Archimedean Solids | trapezohedron | 1.00E-06 | 30 | 246 | 7 | 212 | 252 |

The results above are created by dissecting the particle packing box \([500 200 100] \mu m\) in the 500 x 100 \(\mu m\) plane. 30 vol% of the box is filled with particles. 90 individual slices per particle are processed through ImageJ to retrieve the results (i.e. number of particles and particle area concentration).
Appendix N

Back-of-the-envelope calculation for modeled system

This back-of-the-envelope calculation is used to check the plausibility for the acquired results of the particle packing model and the mathematical representation used is chapter 5. In this calculation, the particle packing results shown in appendix M for *Cube_3000* are used as reference. The final results for this model is presented in figure 5.8 as the hexahedron. Figure N.1 shows the particle including dimensions for *Cube_3000*.

![Figure N.1: Representation of the particle](image1)

The *Cube_3000* particles have a volume of $10^{-6}$ mm$^3$ and from appendix M it can be seen that there are 249 dissected particles per $5 \cdot 10^{-2}$ mm$^2$ ($0.5$ mm x $0.1$ mm).

Figure N.2 represents a damaged coating.

![Figure N.2: Representation of the damaged coating](image2)

In figure N.2 it can be seen that the coating is 0.1 mm thick and contains a scratch with a length of 0.5 mm and an unknown width $dx$. The area of of the damaged coating (at one side) is thus $5 \cdot 10^{-2}$ mm$^2$. 
Appendix N. Back-of-the-envelope calculation for modeled system

The coating has a volume fraction of 0.3 cubical particles. The Delesse’s principle (1848) states that the volume fraction equals the expected area fraction for large systems. This can be confirmed by the results in appendix M. Hence, $1.5 \times 10^{-2} \, \text{mm}^2$ of the in figure N.2 represented scratched area are dissected particles at the surface. The maximum surface area of a single dissected particle is $10^{-4} \cdot \sqrt{2} \, \text{mm}^2$ and the minimum surface area is infinitely small. For this back-of-the-envelope equation the simplification is used that the value will be in the middle, thus $5^{-4} \cdot \sqrt{2} \, \text{mm}^2$. This would mean that there are 212 individual particles dissected the coating per $5 \cdot 10^{-2} \, \text{mm}^2$. This shows that the simple estimation is close to the 249 dissected particles from the model, making the results plausible.

5 vol% of the particle volume ($5 \cdot 10^{-8} \, \text{mm}^3$) relates to the corrosion inhibitor that can be released from the particle. The density of the corrosion inhibitor is 6.77 mg · mm$^{-3}$. Hence, each particle contains 3.4 · 10$^{-7}$ mg corrosion inhibitor. Two sides of the damaged coating will expose 249 particles. Based on the fact that the conditional probability distribution of dissecting a single particle once is 0.5, the simplification is made with the use of the statistical law of large numbers that all the dissected particle together contain halve of the total volume. This results in a total amount of $8.5 \cdot 10^{-5}$ mg corrosion inhibitor that is released from the scratch.

It is assumed that a concentration between $10^{-4}M$ (0.014 mg/ml) and $10^{-3}M$ (0.14 mg/ml) is allowed for for this specific type of corrosion inhibitor to have protection. This means their has to be between $6.1 \cdot 10^{-4} \, \text{ml}$ and $6.1 \cdot 10^{-3} \, \text{ml}$ of electrolyte available at the scratch to reach this concentration with the $8.5 \cdot 10^{-5}$ mg released corrosion inhibitor. Assuming that the electrolyte is only available inside the scratch, the distance $dx$ can be calculated with the known information:

$$dx_{\text{min}} = \frac{6.1 \cdot 10^{-4} \, \text{cm}^3}{0.05 \, \text{cm} \cdot 0.01 \, \text{cm}} = 1.2 \, \text{cm} = 12 \, \text{mm}$$  \hspace{1cm} (N.1)

$$dx_{\text{max}} = \frac{6.1 \cdot 10^{-3} \, \text{cm}^3}{0.05 \, \text{cm} \cdot 0.01 \, \text{cm}} = 12 \, \text{cm} = 120 \, \text{mm}$$  \hspace{1cm} (N.2)

These values are identical to the calculated values as can be seen in figure 5.8 for the hexahedron particles, conforming that there are no calculation mistakes made in the process.
Appendix O

Effect of changing particle size for infinite systems

If we assume two different systems, each having the same volume fraction \( \phi_V \) of uniformly sized particles. The particle radius in system 1 is called \( r_1 \) and the particles in system 2 are called \( r_2 \), both having the same shape. Then the ratio between the two particles radii can be described as

\[
\frac{r_1}{r_2} = \alpha
\]  

(O.1)

The ratio of particle cross-sectional area and volume can simply be described by

\[
\frac{A_1}{A_2} = \alpha^2, \quad \frac{V_1}{V_2} = \alpha^3
\]  

(O.2)

The Delesse’s principle (1848) states that the volume fraction \( \phi_V \) equals the expected area fraction \( \phi_A = \phi_V \) for infinite systems. This also tells us that the volume fraction of dissected particles of system 1 has to equal the volume fraction of system 2

\[
\phi_{V_1} = \phi_{V_2} = \phi_{A_1} = \phi_{A_2}
\]  

(O.3)

In order to know the number of particles (N) exposed when the system is dissected, the total area of dissected particles \( A_{Total} \) has to be divided by the cross-sectional area of the individual particles (assuming that for infinite systems the average particle area is equal to the cross-sectional area), which results in the relation

\[
N_1 = \frac{A_{Total}}{A_1}, \quad N_2 = \frac{A_{Total}}{A_2}
\]  

(O.4)

so

\[
\frac{N_1}{N_2} = \frac{A_2}{A_1} = \alpha^{-2}
\]  

(O.5)

The total volume of all the dissected particles is now simply the number of particles multiplied by their volume, which results in the relation

\[
\frac{N_1 \cdot V_1}{N_2 \cdot V_2} = \alpha = \frac{r_1}{r_2}
\]  

(O.6)

For infinite systems the volume of the particles that are exposed when the system is dissected are directly and linearly related to the particle size size.
Bibliography


Bibliography


