BACHELOR

Comparison between different functional groups and brine compositions on the uptake of dodecane by Surface Engineered Sponges

ten Hacken, Job P.

Award date:
2023

Bachelor End Project

Comparison between different functional groups and brine compositions on the uptake of dodecane by Surface Engineered Sponges

Quartile 3-4 - 2022-2023

Full Name	Student ID	Study
J.P. ten Hacken	1371959	Mechanical engineering

Supervisors: dr. ir. Rücker, M. - ir. Wensink, G.J.

Eindhoven, June 29, 2023

Contents

List of symbols

Symbol	**Definition**	**Unit abbreviation**
Bo	Bond number	-
θ	Contact angle	Rad
κ	Curvature	m^{-1}
ρ	Density	kg/m^3
g	Gravitational acceleration	m/s^2
σ	Interfacial tension	N/m
L	Pore size	m
P	Pressure	Pa
r	Radius	m

1 Introduction

In recent times the world has been dealing with oil pollution problems in wastewater. Oily effluents generated by industries keep contaminating wastewater, which has a significant impact on the environment [1]. As urban development continues to keep growing, the problems caused by oil pollution in wastewater will worsen in the coming years as well [2]. Traditional methods to retrieve oil from the wastewater such as floatation and coagulation have certain disadvantages. The disadvantage of floatation is that it requires high energy consumption, which makes it less environmentally friendly and the disadvantage of coagulation is that it leads to high costs compared to potential newer methods [3]. To clean the wastewater more effectively in the future, newer, innovative methods have to be discovered. Surface Engineered Sponges (SEnS) are recently used to absorb microdroplets of oil from wastewater and have shown promising and environmentally friendly results [4]. SEnS are sponges that are enhanced to have certain surface properties. By using different alternation techniques, the properties of the surface of the sponge can be altered to increase the oil absorption capacity [5]. Research has shown that SEnS can rapidly absorb oil microdroplets with a 95-99% efficiency when a SEnS is placed in an oil-water emulsion, in base, acidic and neutral conditions. [6]. To maximize the potential of the SEnS, it is essential to continue with the development process. The absorption of oil from water by SEnS is caused by multiple different physical mechanisms and is explained further in this chapter.

Wettability

When two fluids, water and oil in this case, are in contact with the sponge, the arrangement of the two phases in contact with the sponge and each other is dependent on an energy balance. In this energy balance, one of the fluids is so-called wetting, and the other fluid is so-called non-wetting. This is dependent on the surface tension between the fluids and the surface. The wetting fluid has more preference to cover the sponge than the non-wetting fluid. Due to this, the interface between the fluids is curved as shown in Figure 1.

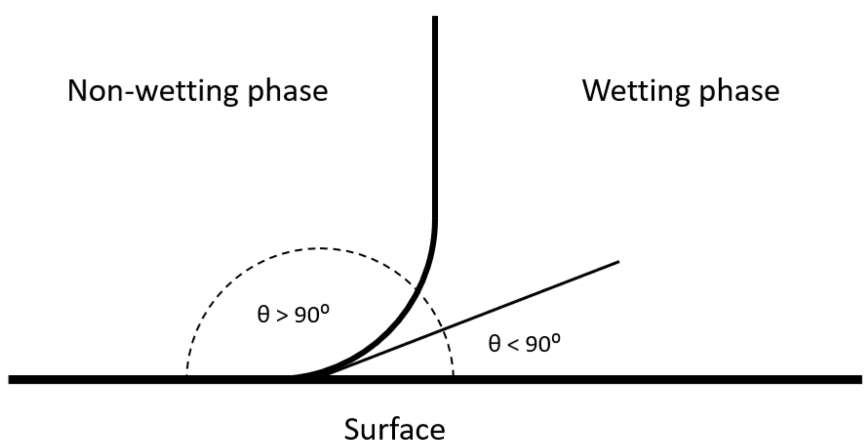


Figure 1: Visualisation of a non-wetting phase and a wetting phase.

This curvature causes a pressure difference between the fluids. In a porous medium, the non-wetting phase has a higher pressure, as it does not want to be next to the sponge and thus requires higher pressure to be forced through the porous medium. The relationship between the pressure difference, between the fluids and the curvature of the interface, is described by the Young-Laplace equation [7], which is described as:

$$P_c = \sigma(\frac{1}{r_1} + \frac{1}{r_2}) = \kappa\sigma \tag{1}$$

Where P_c is defined as the capillary pressure, which is the pressure difference between water and oil, r_1 and r_2 are the different radii of curvature, σ is the interfacial tension between the wetting fluid and the non-wetting fluid and κ is the total curvature. If the curvature is positive, the oil has a higher pressure than the water, if the curvature is negative, the water has a higher pressure. When the fluids are at rest, the capillary pressure is also constant and thus the interface between the fluids has a constant curvature. The radii are able to vary in space, but only when it holds that $\kappa = \frac{1}{r_1} + \frac{1}{r_2}$ for a system of stationary fluids.

By applying a horizontal force balance, the following expression for the contact angle in terms of interfacial tension between the sponge and the two fluids can be found [7]:

$$\sigma_{nws} = \sigma_{ws} + \sigma \cdot \cos\theta \tag{2}$$

Where σ_{nws} represents the interfacial tension between the non-wetting fluid and the sponge, σ_{ws} is equal to the interfacial tension between the wetting fluid and the sponge, σ is the interfacial tension between the wetting fluid and the non-wetting fluid and θ is the contact angle, which is the angle that the interface between the fluid makes with the sponge. The contact angle can have any value between 0 and 180 degrees, as the wetting phase prefers contact with the surface over the non-wetting phase, it always has a contact angle that is smaller than 90 degrees. Thus, when the water contact angle is smaller than 90 degrees, the material can be called hydrophilic. The term wettability is used to refer to the distribution of contact angles throughout the pore space. During the experiments, the sponge is firstly fully saturated with water and then placed in a vessel filled with oil. After the water-saturated sponge is placed in the oil vessel, a two-phase flow occurs that consists of water and oil within the pores, which is caused by the wettability. When the contact angle between the oil and the surface is low, the SEnS is oil wet and it absorbs more oil. Thus creating a SEnS with surface properties causing a very oil-wet situation results in more oil sticking to the sponge fibers. However there is a mitigating factor, when the wetting phase occupies the medium and large sized pores, a disconnected bubble of the non-wetting phase can arise in the centre of a pore [8]. This effect is called residual trapping and can thus reduce the amount of oil absorbed by the sponge, as bubbles of water can get stuck in the pores. An ideal situation is a wettability situation where the sponge is oil-wet, however the water is still able to escape from the pores and be replaced by oil.

Even though wettability is defined as a static property within a multi-phase system, during the process of absorbing oil from the wastewater, the wettability will change over time until the equilibrium point is reached, which is defined by Equation 2. However, as explained, the pore size and shape can cause residual trapping and thus, when looking at individual pores it can be seen that the contact angle differs for each pore [9]. This phenomenon is not only caused by pore size and shape, but also by surface roughness. For each pore, the surface roughness is different and according to the Wenzel model, an increase in surface roughness will decrease the contact angle of the wetting phase [10]. Thus, a higher surface roughness of a SEnS results in a lower contact angle for the wetting phase, inducing a higher oil uptake.

Water salinity

Water salinity has a great impact on the wettability of a surface, over the past years, water flooding has become a popular and cheap method to remove oil from oil reservoirs. Other notable advantages are that it is an environmentally friendly method compared to chemical methods and shows higher oil recovery compared to conventional water flooding [11]. By using low saline water, or water with specific ions, the oil flooding capabilities are improved. Over the past two decades, substantial researches have shown that low salinity water changes the wettability towards a more water-wet state. It has been found that it affects the capillary forces which mainly results in a change of contact angle, and thus wettability, whilst not altering the interfacial tension between the separated oil and water [12]. When looking at the absorption of oil from water by the sponges, the addition of low salinity salts to the brine impacts the absorption in a negative way, as the wettability changes towards a water-wet state, making it more hydrophilic.

Bond number

Another factor that can impact the absorption of oil by sponges is gravity, as water has a higher density than oil. In some situations, gravitational forces can have more impact than capillary forces. The dimensionless Bond number can be calculated with Equation 3 to find the ratio between the gravitational and the capillary forces to find out what impacts the situation most [13].

$$Bo = \frac{\rho g L^2}{\sigma} \tag{3}$$

Where Bo is the dimensionless Bond number, ρ is the density difference between the fluids, g is equal to the gravity, L is equal to the pore size (radius or length) of the porous medium and σ is equal to the surface tension of the interface. When the Bond number is much greater than 1 it indicates that the system is affected more by gravity than by surface tensions. When the number is lower than 1 the surface tensions dominate. Intermediate numbers indicate that both forces impact the system [13].

In this report, experimental data will be analyzed to find out what mechanism has the most impact on the uptake of the oil by a SEnS, and thus the wettability, by creating an automatic analyzing method to process the dynamic CT-scan data. Different results from multiple experiments will be reviewed, where the impact of factors such as the ionic composition of the brine, and functional groups on the SEnS will be compared. These two factors both have their own contribution to the absorption process. The brine composition has an impact on the wettability and the pH value of the water. The sponge type has a direct impact on the interfacial tension between the sponge and the fluids, and the surface roughness, which both impact the wettability.

2 Materials and method

2.1 The experiments

The image data used in the research is obtained from multiple spontaneous imbibition experiments. Spontaneous imbibition is the process by which a wetting fluid is drawn into a porous medium (the sponge) by capillary action [14]. The experiments are 3D visualised using the Environmental Micro-CT system and CoreTom, a multi-resolution 3D X-ray microscope at Ghent University. In total, 6 experiments succeeded. Three tests were done with different sponges using the same brine and three with different brines using the same sponge. The exact details of the experiments can be found in Table 1.

The sponges

In the experiments, three different sponges were tested. A base polyester polyurethane (PU) sponge with pore sizes between 200 and 1100 microns was tested and two different enhanced versions of the PU sponge were tested. The PU sponge is a good base as it has the advantages of high elasticity and elastic recovery and it is relatively lightweight. It can ultimately also provide a large surface area due to the porous 3D structure. The surface of a PU exists of carboxyl and amino groups, which are generally hydrophilic, which is undesired for the purpose of absorbing oil [15]. The contact angle of water on PU sponges is found to be 63 degrees, which confirms the hydrophilicity [16]. Another disadvantage is that PU sponges have high flammability, which can be dangerous when working with crude oil [5].

Figure 2: An image of a water droplet on a PU sponge with a contact angle of 63 degrees [16].

To increase the performance of the sponges, the sponges were enhanced by the addition of a coating. For one of the sponges, a coat of octadecene-capped silicon dioxide (ODA) is added. Octadecene (C18H36) is a molecule with a long chain of hydro-carbon bonds, making the sponge hydrophobic. Thus making it more suitable to absorb oil. For the other sponge, a coat of octadecene amine-capped silicon dioxide (Amin) is added. Octadecene amine (C18H37N1) is an octadecene molecule with an added amine, amines are polar molecules, as nitrogen has a higher electronegativity than carbon and hydrogen combined. This makes them able to interact with dipole water molecules, slightly increasing hydrophilicity. Thus adding solely an octadecene coating would make the sponge a lot more hydrophobic, and adding an octadecene coating amine would also make the sponge more hydrophobic, but less hydrophobic compared to solely adding an octadecene group. For both sponges silicon dioxide was added, which is found to greatly increase the protection of the sponge against wear, making it reusable [17].

The brines

The standard brine is a 0.1M potassium iodide (KI) brine which is used as a contrast agent to get results from the CT-scan as it has a high X-ray absorption due to its atomic weight [18]. In four experiments, only this combination is used. In three experiments, the brine composition was taken as a variable and experiments were conducted with different brine compositions on the Amin sponge. In these experiments, magnesium chloride ($MgCl_2$), sodium sulfate (Na_2SO_4), and sodium bicarbonate ($NaHCO_3$) were added separately. Most brines have a neutral pH value of 7, however, the brine containing sodium bicarbonate has a pH value of approximately 9.7, due to bicarbonate being a weak base.

Table 1: Information about the executed experiments.

Experiment number	Sponge type	Brine composition	Oil
1	PU	KI 0.1M	Dodecane
2	Amin	KI 0.1M	Dodecane
3	ODA	KI 0.1M	Dodecane
4	Amin	KI 0.1M $NaSO_4$ 0.1M	Dodecane
5	Amin	KI 0.1M $NaHCO_3$ 0.1M	Dodecane
6	Amin	KI 0.1M $MgCl_2$ 0.1M	Dodecane

The scans

For each of the 6 experiments, several scans were made during a period of 3 hours. In Table 2, the number of scans and the scan period can be seen. With the scans made at different moments in time, the oil uptake over time can be found. The length of a scan greatly impacts the quality of the scan. For the longer scans, a greatly reduced noise and a bigger difference in voxel intensity for different phases can be identified, which has a big impact on image segmentation and subsequent data processing. Also during a scan fluids shift and cause motion artifacts, which result in blurring in the CT scan results, making it harder to distinguish different phases [19]. However, from looking at the results it is found that the scans taken over a longer period show higher quality results, thus the drawback from the fluids moving provides less impact than the benefits from the longer scan time.

Table 2: Information about the scans made from for each experiment.

Scan period	Scan duration	Amount of scans	Interval
First 10 minutes	2 minutes	5	2 mintes
20 to 60 minutes	10 minutes	4	10 minutes
After 120 minutes	10 minutes	1	-
After 180 minutes	10 minutes	1	-

2.2 Dragonfly

To process the raw image data, Dragonfly 2022.1 is used. Dragonfly is a 3D-image processing program with a lot of different tools that can be used to analyze the images and gain numerical and visual results from the experiments. The most important tools are further explained in this section, more detailed instructions can be found in the Dragonfly Daily tutorials on the Object Research Systems YouTube channel.

Filtering

The first tool used to process the raw image data is filtering. Filtering can be used to clean the images. During a scan, different factors can impact the results and can create noise and image artefacts. For the purpose of this research, a median filter is the best option, as it is known for eliminating noise from images without blurring the edges [20]. A median filter replaces each voxel with the median value of voxels in a certain, definable, range around the voxel and is effective at removing salt-and-pepper noise, which is found in the data. Also in the images, multiple ring artefacts were found, this often occurs due to a defective or miscalibrated detector [21]. By using the 'Ring Artifact' filter in DragonFly, this artefact can be filtered out from the data.

Segmentation

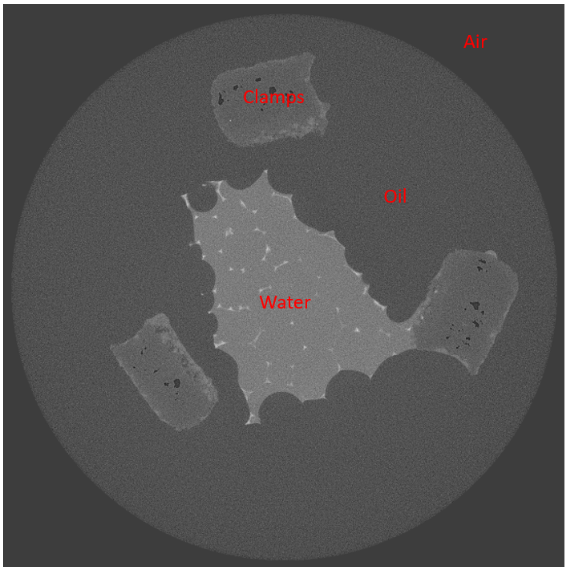
To process data further, segmentation is used to create different Regions Of Interest (ROIs). ROIs can be made of the different phases you can see in the images to distinguish them from the rest of the image. By creating an ROI of a part of the image that is interesting, different numerical properties such as total volume, surface, or amount of loose segmented areas can be extracted from the image. ROIs can easily be created by looking at the grey scale of the voxels, the program can create an ROI with all voxels having a greyness value that is situated between two boundaries. For more difficult segmentations, which occur when for example different phases have equal brightness, or segmentation is hard due to lesser image quality, even after the usage of filters, deep learning segmentation can be used and is used in this research. This was done as regular segmentation did not succeed in processing the data, due to the above-called causes.

Deep learning tool

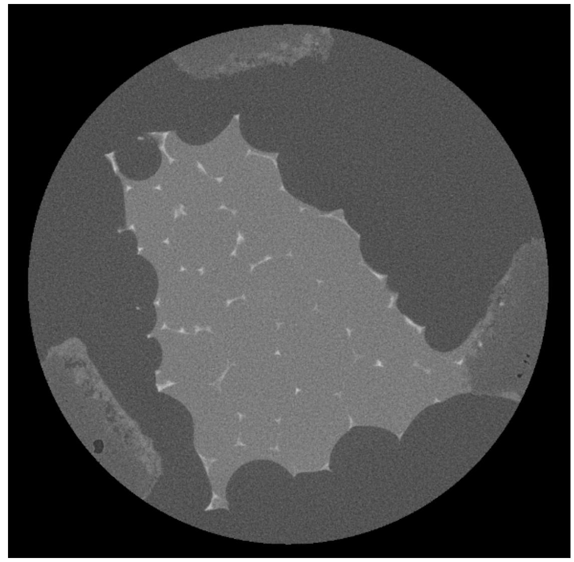
In DragonFly, an easy-to-use tool exists to create a deep learning model to segment images by itself. To get this working, a model has to be trained with self-made training data to be able to identify objects according to your instructions. As 3D images can exist out of more than 1000 different slices, this method is very useful and saves a lot of time.

2.3 Obtaining the segmented data

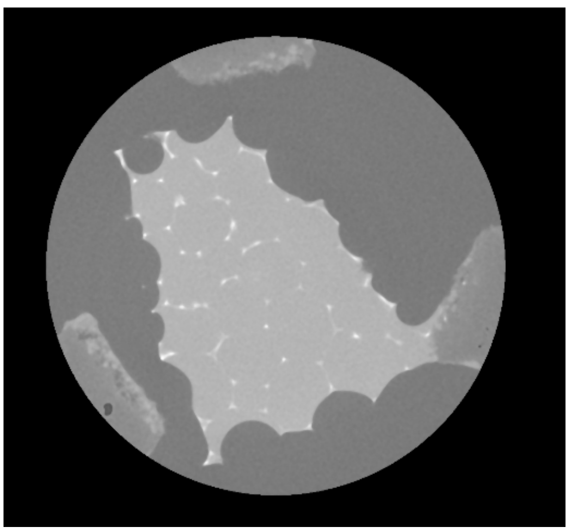
The scans were made of a more extensive area where the sponges, for most scans, were situated in the middle of the scan. As the sponges are smaller than the area covered by the scan, the scans contained big areas that were filled with oil that did not move during the whole observed experiment. Thus to make the process of filtering and segmentation more efficient and less time-consuming, whilst attaining the same results, images were cropped such that only the relevant parts remained. The cropped images were then filtered with a median filter with a size of 7, which means that the pixel takes the median of the grey value of all pixels in a cube, with a diagonal length of 7, around the pixel. The next step is to create the training data for the deep learning model, different training data sets were created by hand which were used to train the deep learning model. After training the model with a few datasets, it can be tested whether the model is trained correctly. A preview can be generated of the slice that is currently looked at and it can be seen whether segmentation is done correctly, at a certain point the model is able to create segmentations with a small error. These segmentations can be altered again by hand to use them as extra training data to optimize the model up to a point where the error is as little as possible. This is useful as generating and correcting a preview is less time-consuming than creating a whole slice of training data by hand. When the deep learning model is able to create correct segmentations of different slides, the model can be run to create a segmentation of the whole scan. For the different scans, different models were trained, due to differing image qualities, grey scales, and overall pixel brightness division within scans, training a single model to segment all the images did not succeed. A trained model for a specific scan gave wrong segmentation results for another scan. In Figure 3, the process described above is visualized.



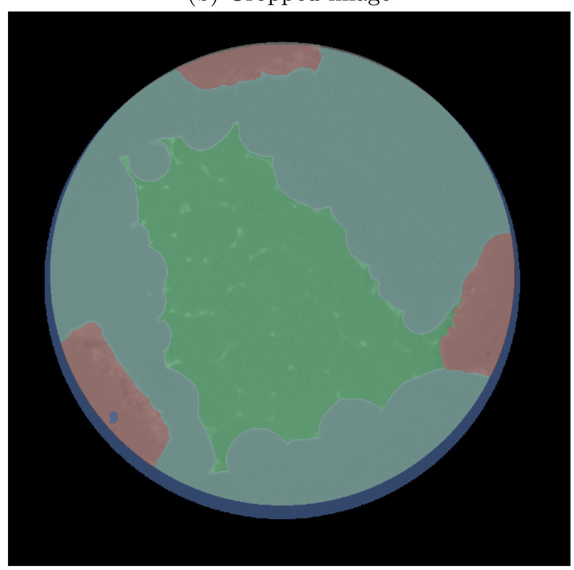
(a) Raw scan slice



(b) Cropped image



(c) Filtered image



(d) Segmented image

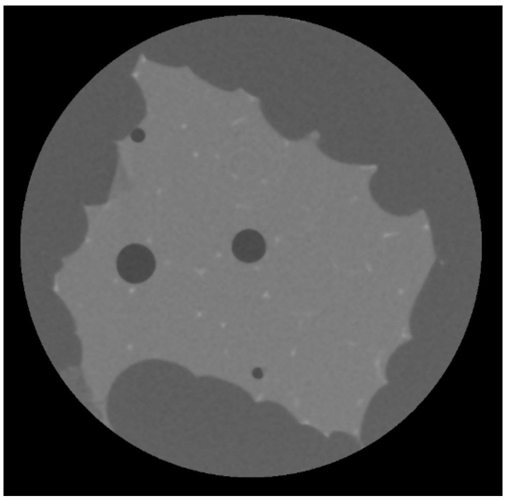
Figure 3: Process of obtaining the result data.

The segmented data can then be used to get multiple sorts of results. By looking at the amount of voxels of water in the scans, which is represented by the amount of voxels in the ROI, the water volume can be determined overtime. As the experiments are conducted in a closed environment with water and oil, the reduction in water volume in the sponges has a direct relation to the amount of oil that is infiltrating the sponge. By determining a relative number, thus comparing the volume over time to the starting volume, the results can be normalized and compared between the different experiments. By comparing the segmentations of the experiments at different moments in time, the way the oil infiltrates the sponge can be visualized and analyzed. Those two types of results are shown in the next chapter.

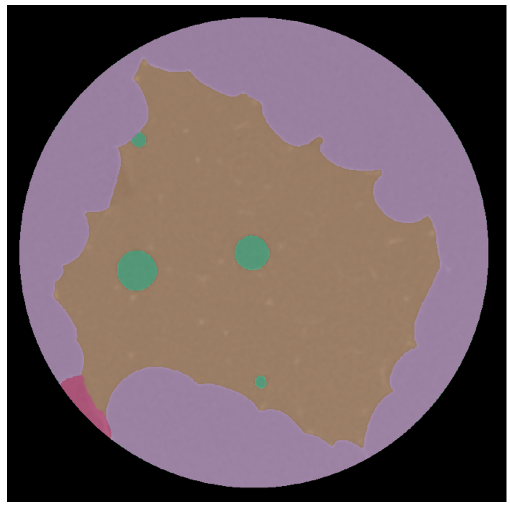
3 Results and discussion

3.1 Segmentation validation

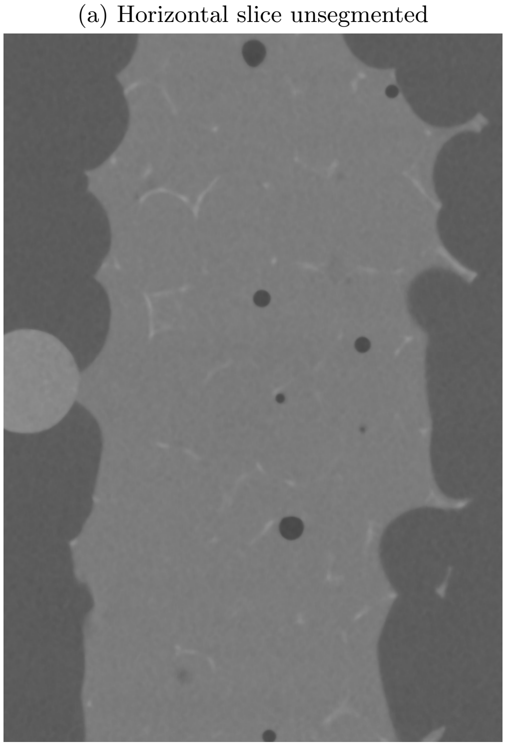
To use the results obtained after using the deep learning segmentation tool it is important to validate whether the results are correct. As the results from the deep learning tool show a segmented image, it could be checked whether the segmentations were correct. For this reason, the results were validated by eye. A validation example is shown in Figure 4, where it can be seen that the different phases are correctly segmented by the deep learning tool.



(a) Horizontal slice unsegmented



(b) Horizontal slice segmented



(c) Vertical slice unsegmented

(d) Vertical slice segmented

Figure 4: Example of validation.

3.2 Numerical results

Different sponges

As described before, tests were conducted with the PESPU, ODA, and Amin sponges on absorbing dodecane during the spontaneous imbibition experiment with the sponge filled with the KI brine. In Figure 5 the normalized water content within the sponge is shown over time. The normalized water content describes how much water is replaced by oil during the experiment. From this data, the absorption capabilities of different sponges can be found and compared. From the graph can be concluded that the Amin sponge achieved the largest water content reduction during the experiment, closely followed by the ODA sponge. This result was not directly expected, as the ODA sponge is more hydrophobic. However, something to be noted is that during the first few minutes of the experiment, the water volume in the ODA sponge raises before it started going down, which impacts the final result. This is caused by gravity, which is broken down further in Subsection 3.3. Also, the reduction in water volume is still present between the 120-minute and 180-minute marks, which indicates that the final equilibrium position might not be reached yet. Results from Amott tests conducted in another research show that it can take up to two weeks before a SEnS has reached a wettability equilibrium position [22]. They also show that after a period of 3 hours, the total water loss is approximately 30% of the final equilibrium water loss, indicating that results can still change a lot. Experimenting for a longer period of time can thus show different results. The results also show that the PESPU sponge absorbs no oil, which is as expected as PU sponges are hydrophilic.

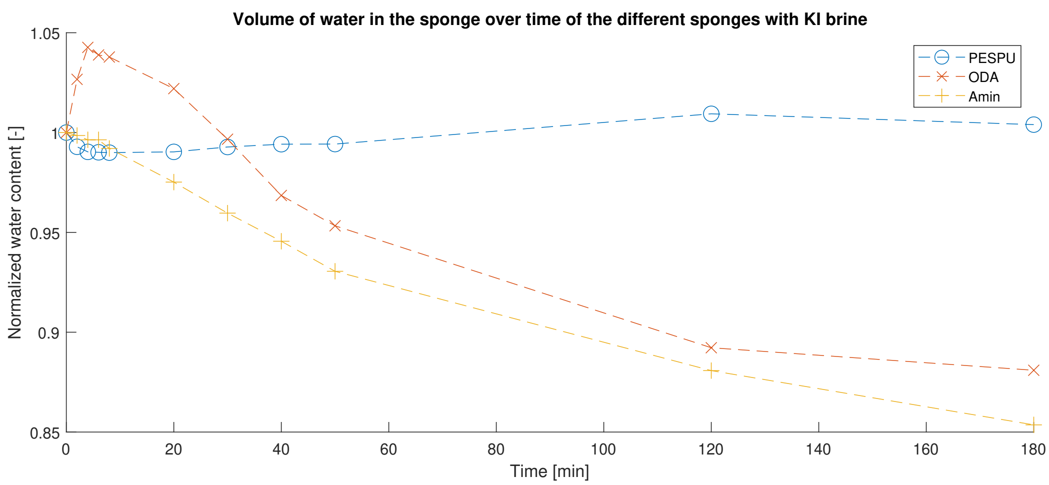


Figure 5: Relative water volume in the sponge over time of the different brines on Amin sponge.

Different brines

In all the tests KI is added to the water to be able to distinguish the water from the oil in the CT scans, the impact of the addition of KI on the wettability cannot be found from this research, however, it surely has an impact. Research on SEnS has shown that adding a 0.1M KI brine, instead of a NaCl brine, impacts the results from a CT scan unexpectedly [22]. Instead of the water being darker, due to the higher molar mass of the brine, the fibres appear darker than the water. This indicates that the sponge adsorbs iodide ions instead of oil, which it is not designed for. The SEnS contains chlorine, carboxylic and amine groups, which can cause the sponge to adsorb the iodide ions. As the sponge used in these experiments is also coated with an amine group, the addition of KI ions can cause the sponge to adsorb the iodide ions. Due to the adsorption of the iodide ions, which are only located in the water and not in the oil, the wettability can potentielly change to a more water-wet state which will decrease the uptake of oil.

Tests were also conducted with different brines, containing KI, on the Amin sponge. In Figure 6, which shows the normalized water content within the sponge over time for the different brine compositions. It can be seen that the test conducted with the potassium iodide brine shows the largest water content reduction during the experiment, followed by the $KI + Mg_2Cl$ brine experiment and the $KI + NaHCO_3$ brine experiment, which all succeed to absorb dodecane during the experiment. Results also show that the experiment conducted with the $KI + NaSO_4$ brine starts with an increase in water volume, but after an hour, the volume starts going down which in the end led to no oil being absorbed after 3 hours, what exactly happens here is broken down further in Subsection 3.3.

As explained in the introduction, previous research on the effect of brine type on the wettability alteration has shown that low-salinity brines can alter the wettability of a surface from oil-wet to water wet. In more specific research on the impact of different brines on the oil-water wettability on naphthenic-acid-adsorbed calcite surfaces more specific information on the ions used in this research is found [23]. Naphthenic-acid-adsorbed calcite is a different material than used in this experiment. However, what both materials have in common is that both amine groups, which are found on the SEnS, and carboxylic acids, found in the naphthenic acid, can bond with the ions in the brines and alter the wettability.

This research shows that the lowest oil contact angle values were obtained for 0.164M NaCl or Na_2SO_4 solutions, which indicates that the presence of SO_4^{2-}, or reduction in NaCl concentration induces a wettability alteration towards a water-wet state. Previous research also showed that $MgCl_2$ over NaCl and $MgSO_4$ over Na_2SO_4 show less wettability alteration, suggesting that Mg^{2+} ions show less wettability alteration than Na^+ ions [23]. A different research measured the zeta potential, which is related to surface charge, on different natural carbonates [24]. The research found that a 0.1M $MgCl_2$ brine has a 3 times higher zeta potential than a 0.1 M $NaCl_2$ brine for Iceland Spar, the tested material. The lesser wettability alteration could be caused by the higher positive surface charge for $MgCl_2$. This could also be the reason for the results found in this research, however it cannot be said for sure as the material is different.

In the results from this research, it is found that the addition of $MgCl_2$ to the brine slightly decreases the oil uptake, but not as much as the other salts. The addition of Na_2SO_4 drastically alters the wettability towards a water-wet state, decreasing the oil uptake by a lot. Which results in no oil adsorption. The addition of $NaHCO_3$ decreases the uptake more than the addition of $MgCl_2$ and less than the addition Na_2SO_4, as Na^+ ions show more wettability alteration than Mg^{2+} ions. From the results it can be concluded that the HCO_3^- ions provoke less wettability alteration to a water-wet state than the SO_4^{2-} ions. Previous research also found a negative zeta potential with the presence of SO_4^{2-} ions for Iceland Spar, where the negative zeta potential could be the reason for the wettability alteration to a water wet state [24].

Something else to be noted from Figure 6 is that the sodium bicarbonate scan shows no oil adsorption between 50 and 120 minutes, this will be researched in Subsection 3.3.

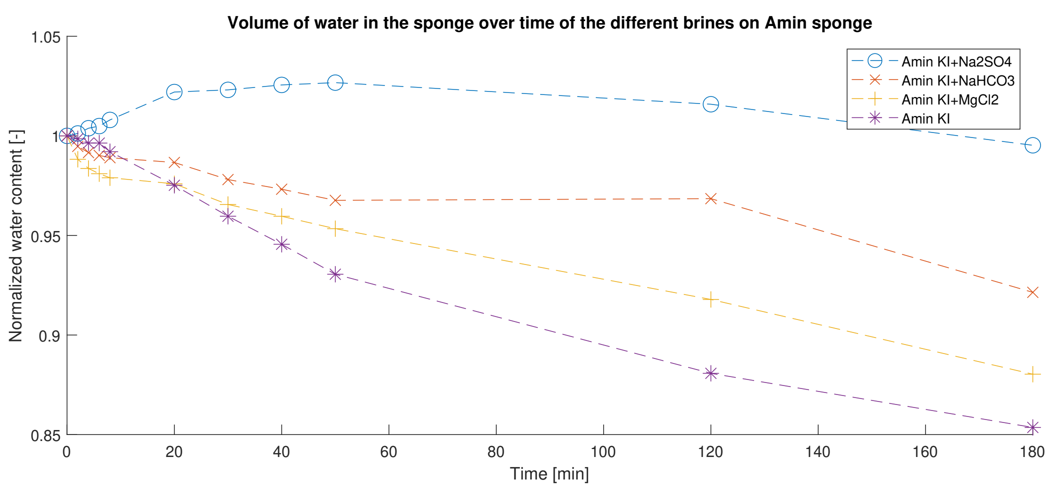


Figure 6: Relative water volume in the sponge over time of the different brines on the Amin sponge.

3.3 Visual results

The segmentation results from the deep learning tool can be used to analyze how the oil infiltrated the sponge, in this subsection, a few notable results from the numerical results are analyzed by looking at the visual data. In Figure 7, the infiltration of oil in the Amin sponge with the pure KI brine is shown to demonstrate the regular infiltration of oil without special occasions.

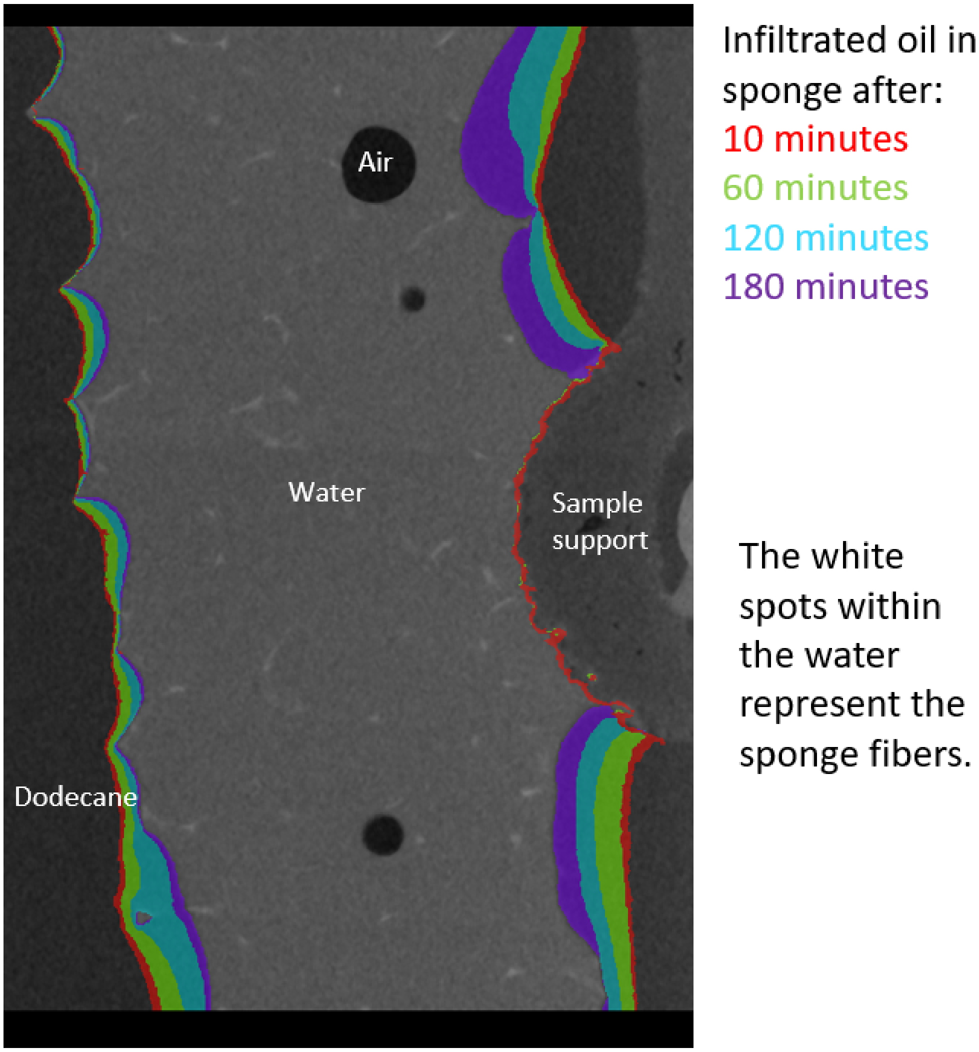
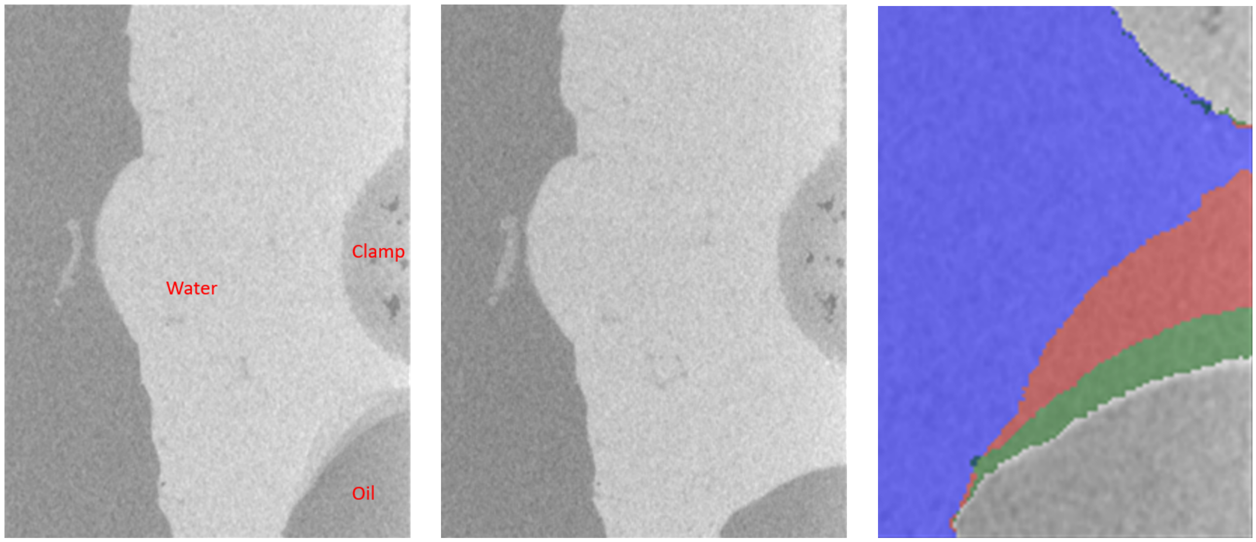


Figure 7: Infiltration of oil in a sponge during an entire scan.

ODA sponge

As mentioned before, the water volume within the ODA sponge raises during the first 5 minutes of the experiment. When a look is taken at the visual data, it can indeed be seen that the volume of water increases. In Figure 8a and Figure 8b vertical slices of the first and 4-minute scan are shown, where it can be seen that the water volume increases, whilst the oil volume decreases in the bottom right corner. Also in Figure 8c, the blue ROI indicates the initial area covered by water, whilst the red ROI shows the extra area covered by water after 2 minutes, and the green ROI shows the extra area covered by water after 4 minutes.



(a) 0 minute scan (b) 4 minute scan (c) Water difference 0-2-4 minutes

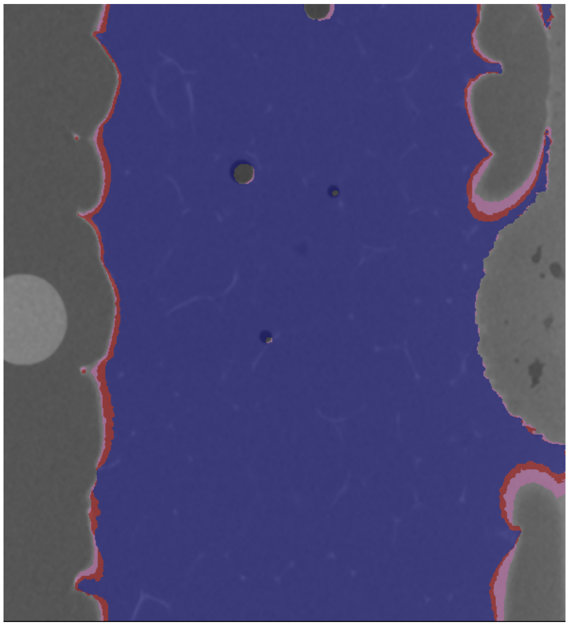
Figure 8: Vertical slices of the ODA scan.

This only occurs at the interface between the water and the oil is (slightly) horizontal. As the density of dodecane is equal to 750 kg/m^3, which is lower than the density of water, which is 998 kg/m^3, this effect seems to be caused by gravity. By applying Equation 3, the Bond number is calculated. By using the following numerical data: a density difference of 248 kg/m^3, gravitational acceleration of 9.81 m/s^2, a pore size of 200-1100 microns, and a surface tension between water and dodecane of 52.87 mN/m. The Bond number is then calculated to lie between 9.2 and 50, due to the diverse range in pore sizes. This number is higher than 1, which confirms that gravitational forces indeed play a role in the experiments.

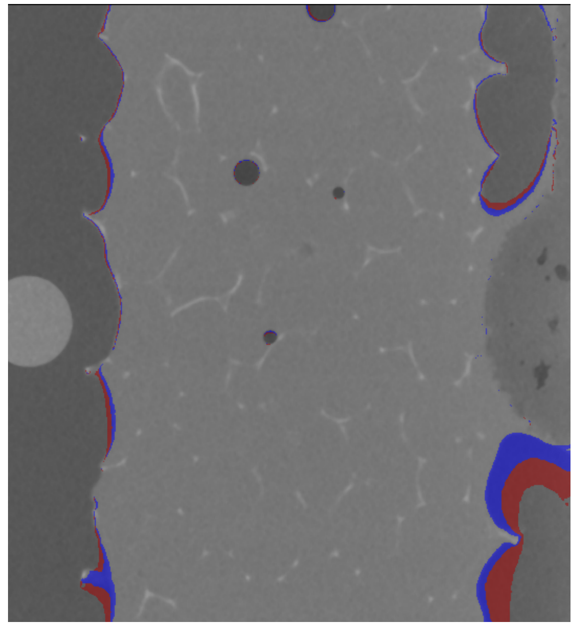
Sodium sulfate scan

In the numerical data of the sodium sulfate scan it was found that the relative water volume increases during the first hour and then drops back down again to the initial volume. In the test with the ODA sponge, a raise in relative water volume was also found, however, that only lasted a few minutes instead of an hour. In Figure 9a, the water volume of a vertical slice of the sponge at different timestamps is shown. The blue ROI displays the area covered by water found in the first scan, and the red ROI displays the difference in the area that the water covers between the first scan and the 8-minute scan. The pink ROI displays the difference in the area that the water covers between the 8-minute and the 50-minute scan. The scan in the background is the 50-minute scan. In the scans, most oil-water interfaces are vertical, however, the scan location in this test is different. Most scans are made higher and two rings are present in these scans. However this scan is made of a lower area, which can be seen by the ring being located in the middle. Thus although the lack of horizontal surfaces, water located in the area above the scan area is pushed downwards by gravity and causes the water within the scan area to infiltrate the sponge, causing the increase in water area.

In Figure 9b, the oil infiltration in the sponge is analyzed for the rest of the experiment. Where the red shows the water area infiltrated by oil between 50-120 minutes and the blue ROI shows the water area infiltrated by oil between 120-180 minutes. From this, it can be seen that the oil actually starts infiltrating the sponge after the 50 minutes scan, which confirms the numerical data. This indicates that the contribution of gravity is finished and the oil is now absorbed by the sponge. However, it still results in very low oil absorption. This confirms that the Na_2SO_4 drastically alters the wettability towards a water-wet state.



(a) Water volume after 0, 8 and 50 minutes

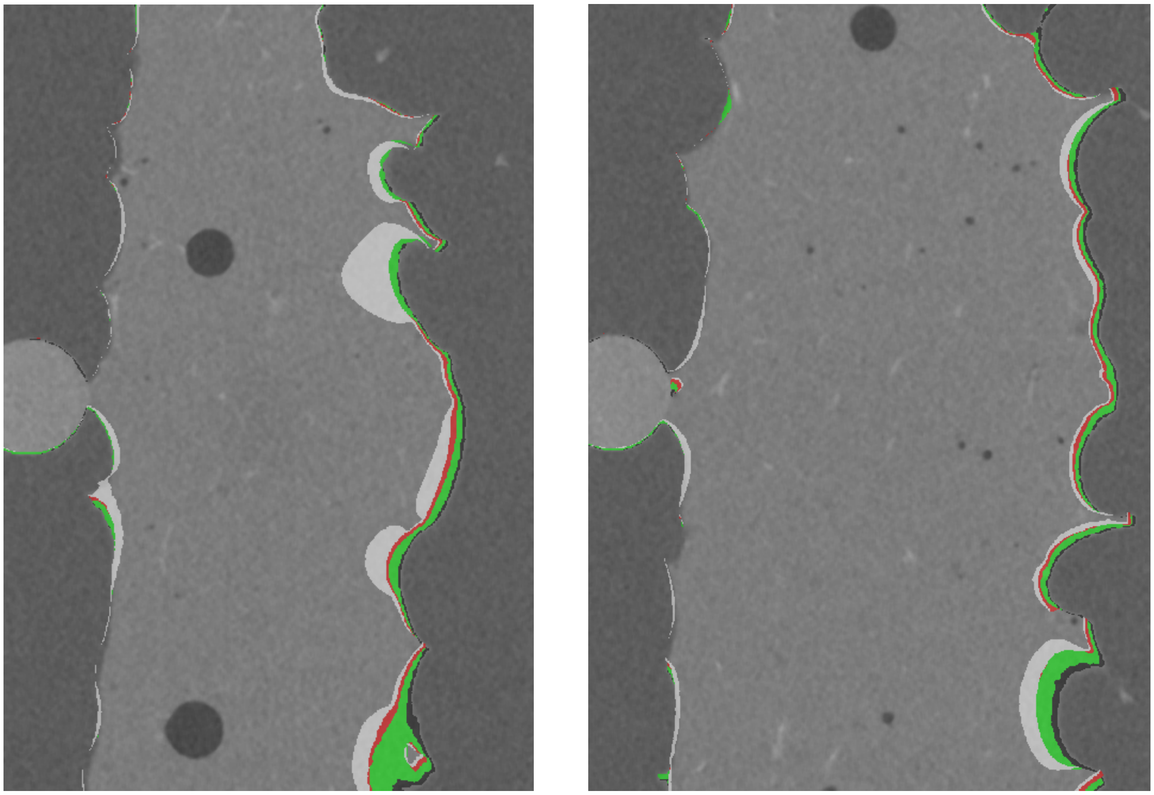


(b) Oil infiltration between 50-120/120-180 minutes

Figure 9: Vertical slice of the area covered by water in sodium sulfate experiment at different timestamps.

Sodium bicarbonate scan

In the numerical data of the sodium bicarbonate scan it was found that over the period of the whole experiment the water volume shrunk, however between the 50-minute and the 120-minute scan the volume stayed constant. To confirm that this is no mistake, a look was taken at the visual data. In Figure 10, two vertical slices in the sponge are displayed. The black ROI displays the oil that infiltrated the sponge within 10 minutes, the green ROI displays the oil that infiltrated the sponge between 10-60 minutes, the red ROI displays the oil that infiltrated the sponge between 60-120 minutes and the white ROI displays the oil that infiltrated the sponge between 120-180 minutes. From this data, it can clearly be seen that the red area is very small, whilst the white and green areas cover a lot bigger space. This confirms that the oil indeed had very low infiltration during the period of 60 to 120 minutes of the experiment, which shows that adsorption of oil also happens after long periods of time, indicating that conducting an experiment over a longer period than 180 minutes might show different end results.



(a) Oil infiltration in the sponge

(b) Oil infiltration in the sponge 2

Figure 10: Oil infiltration in two vertical slices of the experiment with sodium bicarbonate.

4 Conclusion

The purpose of this research was to find out which mechanism has the most impact on the uptake of oil by a SEnS. 3D CT scans from multiple spontaneous imbibition experiments were analyzed in Dragonfly 3.0, using a self-trained deep learning model to find numerical information about the amount of water that was exchanged for oil, and visual information to find out more about the dynamic behaviour of the oil infiltrating the sponge.

From the experiments conducted to find out whether the PESPU, ODA or Amin sponge would succeed best in absorbing oil, the Amin sponge showed the best highest oil uptake after the testing period of 180 minutes. Closely followed by the ODA sponge. This result was not exactly as expected, as the ODA sponge is more hydrophobic, which should attract more oil. However, this experiment was affected by gravitational forces due to a horizontal water-oil interface within the sponge, which led to an increase of almost 5% in water volume during the first 5 minutes of the test. The experiment on the Amin sponge was not influenced by this mechanism, giving it an advantage compared to the ODA sponge experiment. The PESPU sponge showed no oil adsorption, as the PESPU sponge is hydrophilic. From these results, it can be concluded that the addition of the hydrophobic coatings greatly increased the oil adsorption capabilities of the initial PESPU sponge. Also, it can be concluded that gravity can greatly impact the amount of oil that is absorbed by the sponge for experiments conducted over a period of 3 hours.

From the experiments conducted to find the difference in the impact between the addition of 0.1M $MgCl_2$, Na_2SO_4 or $NaHCO_3$ to the initial 0.1M KI brine it was found that the addition of each of the salts to the brine would decrease the ability of oil absorption. In the scan with the initial brine, the largest amount of initial water volume is replaced by oil. The addition of $MgCl_2$ showed little decrease in absorption. The addition of $NaHCO_3$ showed a higher decrease in absorption than the addition of $MgCl_2$ and the addition of Na_2SO_4 led to no oil being absorbed. These results were similar to results found in previous research. When a look is taken into the visual data, the brine containing Na_2SO_4 showed it initially absorbed water due to gravity, whilst later changing to a state where the sponge absorbs oil. However, due to the experiment time of only 3 hours, it cannot be known whether the sponge continues to absorb oil or stabilizes. From this, it can be concluded that the ion type greatly impacts the wettability and thus, the adsorption of oil by the sponge. As even tho the Amin sponge is initially hydrophobic, the addition of specific ions to the brine can cause the sponge to fail in the absorption of oil. Previous research also found that the addition of KI to the brine, instead of NaCl, can cause the sponge to adsorb iodide ions, which are located in the water, and thus decrease the absorption of oil.

Overall, the conclusion can be drawn that the addition of a hydrophobic coat is required for the sponge to absorb oil, the surface tension of the sponge greatly impacts the wettability and thus, the oil uptake of the sponge. Amin is found to absorb the most oil and ODA slightly less. However, the 5% increase in water volume at the beginning of the test due to gravity greatly affected the final result ODA test. The usage of specific ions can greatly impact the oil uptake of the sponge and impact the absorption and can even cause hydrophobic sponges to not absorb oil at all, where the usage of a 0.1M KI brine led to the highest oil uptake.

To improve the results of new research, the following things could be done differently. Conducting tests over an extended period of time, until an equilibrium position is reached, which can take up to 14 days. This is needed as results from multiple tests show that the volume of the water in the sponge is still going down, which can still have a big impact on the outcome of the tests. Also by conducting spontaneous imbibition experiments with only vertical water-oil interfaces, a similar gravitational influence can be found in the results, which results in a direct comparison between the impact of the brine types and the functional groups on the sponges, without undesired factors influencing the results.

References

[1] A. D. M. d. Medeiros, C. J. G. d. Silva Junior, J. D. P. d. Amorim, I. J. B. Durval, A. F. d. S. Costa, and L. A. Sarubbo, "Oily Wastewater Treatment: Methods, Challenges, and Trends," *Processes*, vol. 10, p. 743, 4 2022.

[2] E. K. Sam, J. Liu, and X. Lv, "Surface Engineering Materials of Superhydrophobic Sponges for Oil/Water Separation: A Review," *Industrial & Engineering Chemistry Research*, vol. 60, pp. 2353–2364, 2 2021.

[3] R. Sarkhel and P. Ganguly, "Oil pollution and municipal wastewater treatment: issues and impact," in *Advances in Oil-Water Separation*, pp. 57–64, Elsevier, 2022.

[4] Z. Zhang, G. Sèbe, D. Rentsch, T. Zimmermann, and P. Tingaut, "Ultralightweight and Flexible Silylated Nanocellulose Sponges for the Selective Removal of Oil from Water," *Chemistry of Materials*, vol. 26, pp. 2659–2668, 4 2014.

[5] N. Y. Abu-Thabit, O. J. Uwaezuoke, and M. H. Abu Elella, "Superhydrophobic nanohybrid sponges for separation of oil/ water mixtures," *Chemosphere*, vol. 294, p. 133644, 5 2022.

[6] P. Cherukupally, W. Sun, A. P. Y. Wong, D. R. Williams, G. A. Ozin, A. M. Bilton, and C. B. Park, "Surface-engineered sponges for recovery of crude oil microdroplets from wastewater," *Nature Sustainability*, vol. 3, pp. 136–143, 12 2019.

[7] M. J. Blunt, *Multiphase Flow in Permeable Media*. Cambridge University Press, 10 2016.

[8] A. Alhosani, B. Bijeljic, and M. J. Blunt, "Pore-Scale Imaging and Analysis of Wettability Order, Trapping and Displacement in Three-Phase Flow in Porous Media with Various Wettabilities," *Transport in Porous Media*, vol. 140, pp. 59–84, 10 2021.

[9] B. Xiong, J. Li, C. He, X. Tang, Z. Lv, X. Li, and X. Yan, "Effect of pore morphology and surface roughness on wettability of porous titania films," *Materials Research Express*, vol. 7, p. 115013, 11 2020.

[10] K. Kubiak, M. Wilson, T. Mathia, and P. Carval, "Wettability versus roughness of engineering surfaces," *Wear*, vol. 271, pp. 523–528, 6 2011.

[11] H. Ben Mahmud, S. Arumugam, and W. Mahmud, "Potential of Low-Salinity Waterflooding Technology to Improve Oil Recovery," in *Enhanced Oil Recovery Processes - New Technologies*, IntechOpen, 12 2019.

[12] P. Rostami, M. F. Mehraban, M. Sharifi, M. Dejam, and S. Ayatollahi, "Effect of water salinity on oil/brine interfacial behaviour during low salinity waterflooding: A mechanistic study," *Petroleum*, vol. 5, pp. 367–374, 12 2019.

[13] D. Or, M. Tuller, and S. B. Jones, "Liquid Behavior in Partially Saturated Porous Media under Variable Gravity," *Soil Science Society of America Journal*, vol. 73, pp. 341–350, 3 2009.

[14] N. R. Morrow and G. Mason, "Recovery of oil by spontaneous imbibition," *Current Opinion in Colloid & Interface Science*, vol. 6, pp. 321–337, 8 2001.

[15] S. M. Kong, Y. Han, N.-I. Won, and Y. H. Na, "Polyurethane Sponge with a Modified Specific Surface for Repeatable Oil–Water Separation," *ACS Omega*, vol. 6, pp. 33969–33975, 12 2021.

[16] L. Liang, Y. Xue, Q. Wu, Y. Dong, and X. Meng, "Self-assembly modification of polyurethane sponge for application in oil/water separation," *RSC Advances*, vol. 9, no. 69, pp. 40378–40387, 2019.

[17] J. Guo, C. Wang, H. Yu, and X. Li, "Preparation of a wear-resistant, superhydrophobic SiO2/silicone-modified polyurethane composite coating through a two-step spraying method," *Progress in Organic Coatings*, vol. 146, p. 105710, 9 2020.

[18] P. van Hemert, E. S. J. Rudolph, and P. L. Zitha, "Micro Computer Tomography Study of Potassium Iodide Precipitation in Bentheimer Sandstone Caused by Flow-through CO2 Drying," *Energy Procedia*, vol. 37, pp. 3331–3346, 2013.

[19] A. Murphy, "Motion artifact," in *Radiopaedia.org*, Radiopaedia.org, 10 2016.

[20] Y.-P. Wang, Q. Wu, and K. R. Castleman, "Image Enhancement," in *Microscope Image Processing*, pp. 55–74, Elsevier, 2023.

[21] A. Ramasamy, B. Madhan, and B. Krishnan, "Ring artefacts in cranial CT," *BMJ Case Reports*, pp. 2018–226097, 8 2018.

[22] K. D. Van Kempen and M. Rücker, "Translating digital rock imaging techniques to the analysis of pore-scale wetting of foams to bridge the gap between molecular interactions and macro-scale wetting Master Thesis," tech. rep.

[23] I. Shaik, J. Song, S. Biswal, G. Hirasaki, P. Bikkina, and C. Aichele, "Effect of brine type and ionic strength on the wettability alteration of naphthenic-acid-adsorbed calcite surfaces," *Journal of Petroleum Science and Engineering*, vol. 185, p. 106567, 2 2020.

[24] M. İlhan, H. E. Gültekin, S. Rençber, Z. Şenyiğit, and H. H. Aydın, "Aquasomes: a novel platform for drug delivery," in *Systems of Nanovesicular Drug Delivery*, pp. 191–206, Elsevier, 2022.

Appendices

A Matlab code for the numerical result plots

```
%% scan 2
med_2 = [283338925 281319387 280600522 280538207 280489312 280598727 281291176 281688087 ...
    281706859 286000678 284465405];
time = [0 2 4 6 8 20 30 40 50 120 180];
%% scan 3
med_3 = [315540431 315126923 315019052 312528309 308658773 305355311];
%% scan 4
med_4 = [260335519 267275438 271441597 270455559 270187740 266064146 259468116 252134898 ...
    248178115 232278130 229340347] ;
%% scan 5
med_5 = [416173862 416650663 417697932 418132565 419358929 424932963 425366586 426352126 ...
    426811629 422494721 414289763] - 18115606;
%% scan 8
med_8 = [236667768 235456975 234751294 234425897 234164141 233614436 231655273 230546241 ...
    229273110 229466781 218725049] - 8297310;
%% scan 9
med_9 = [315364527 311653870 310200525 309370501 308729380 307773854 304496690 302628924 ...
    300665373 289459663 277625483];
%% scan 12
med_12 = [318837231 318367783 317681449 317681449 316299541 310925285 305970201 301481270 ...
    296683351 280822385 272158987];
%% Sponges
figure()
hold on
plot(time,med_2/med_2(1),'--o','MarkerSize',10)
plot(time,med_4/med_4(1),'--x','MarkerSize',10)
plot(time,med_12/med_12(1),'--+','MarkerSize',10)
legend('PESPU', 'ODA', 'Amin')
ylabel('Normalized water content [-]')
xlabel('Time [min]')
title('Volume of water in the sponge over time of the different sponges with KI brine')
%% Brines
figure()
hold on
plot(time,med_5/med_5(1),'--o', 'MarkerSize',10)
plot(time,med_8/med_8(1),'--x','MarkerSize',10)
plot(time,med_9/med_9(1),'--+','MarkerSize',10)
plot(time,med_12/med_12(1),'--*','MarkerSize',10)
legend('Amin KI+Na2SO4', 'Amin KI+NaHCO3', 'Amin KI+MgCl2', 'Amin KI')
ylabel('Normalized water content [-]')
xlabel('Time [min]')
title('Volume of water in the sponge over time of the different brines on Amin sponge')
```

B Scientific conduct

Declaration concerning the TU/e Code of Scientific Conduct for the Bachelor's Final Project

I have read the TU/e Code of Scientific Conduct[i].
I hereby declare that my Bachelor's final project has been carried out in accordance with the rules of the TU/e Code of Scientific Conduct.

Date

29-6-2023 ……………………………………………..…………..

Name

Job Peter ten Hacken ……………………………………….………

ID-number

1371959 …………………………………………………..…………..

Signature

Job Peter ten Hacken …………………………………………………..…………..

Type text here

See:
The Netherlands Code of Conduct for Scientific Integrity, endorsed by 6 umbrella organizations, including the VSNU, can be found here also. More information about scientific integrity is published on the websites of TU/e and VSNU.