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PDEng - Chemical Product Design

Individual Design Project

Design of a Gel Product for sedimentation control in the Rotterdam port area

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Summary

Sediment tends to accumulate in small channels in port of Rotterdam which obstructs daily ship navigation and as a result needs to be removed by high-cost dredging operations. The goal of this project was to design a gel product that helps in the sedimentation control in the Rotterdam port area and contributes to the reduction of disposal costs, by offering a feasible, stable and eco-friendly solution. The following steps were followed:

- Technoeconomic evaluation to identify the materials and recipe
- Stability trials to determine critical rheological factors and provide data for CFD study
- Product and application concepts
- Feasibility investigation for the use of Kaumera as a gelation agent and other applications

Six alternative product structures were identified as possible solutions in different port locations for sedimentation control and were evaluated against set criteria. Specifically for the gel barrier project, Xanthan gum and fine sediment were combined to provide a stiff gel in port areas with speed currents <0.1 m/s. A sensitivity analysis took place, considering material, manufacturing, application and transportation costs. The results indicate that 1 M€/y can be spared by making 10 gel barriers/y in the entrance of Botlek, provided that the barrier will prevent 45% of incoming sediment.

The inline preparation of the gel barrier was proven to be the most economically feasible application strategy. With the proposed method, the CO_2 emissions associated with dredging can be reduced by 40%, saving up to 2400 t CO_2/y. The trade-off of designing a biodegradable product is the lower lifetime of the barrier.

Building a barrier in the port seems a promising application for cost and CO_2 reduction and cost-effective trials could be made to validate the barrier's efficiency in reducing incoming mud.

With the current recipe the barrier's lifetime is around 4 weeks, thus the recipe and reduction in incoming sediment should be further optimized. As a follow up of this project an ongoing CFD study will show if the barrier can stay in place based on the hydrodynamic conditions in the port. A roadmap for the project development includes prolonging the efficiency of the gel in reducing dredging costs, performing large-scale trials in Deltares flume to test the efficiency and finally a pilot scale trial in port of Rotterdam.

Special emphasis was made on the use of Kaumera in port applications. Due to its complex composition, utilizing Kaumera in a gel barrier requires a more in-depth analysis. However, Kaumera's technical characteristics can be improved when combined with Xanthan gum or clays at optimal ratio and pH. Bio-flocculation is a promising application for rewetted dried Kaumera and its use in the port could potentially have a positive impact on the water ecosystem.

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Abbreviations

BO: Botlek

BOD: basis of design

CMC: Carboxyl methyl cellulose

CTIG: Civiele Techniek en Geowetenschappen

EP: Europoort

EW: Eem/Waalhaven

GG: Guar gum

LOD: Loss on drying

MV: Maasvlakte

MW: Molecular Weight

PAA: Polyacrylic Acid

PDEng: Professional Doctorate in Engineering

PN: Pernis

PoR: Port of Rotterdam

SPM: Suspended Particulate matter

WID: Water Injection Dredging

XG: Xanthan gum

Chapter 1: Introduction

1.1. Project background

The port of Rotterdam (PoR) is the biggest port in Europe and the largest point for import and export of goods in Europe in 2020. The total cargo that has been handled last year surpasses 400 million tones and includes dry and liquid bulk material, as well as containers. The port covers an area greater than 100 km^2 extending from the city of Rotterdam to Maasvlakte (Port of Rotterdam Authority, 2020). The map on Figure 1.1 shows the regions (in orange) where the main activities of the port take place.

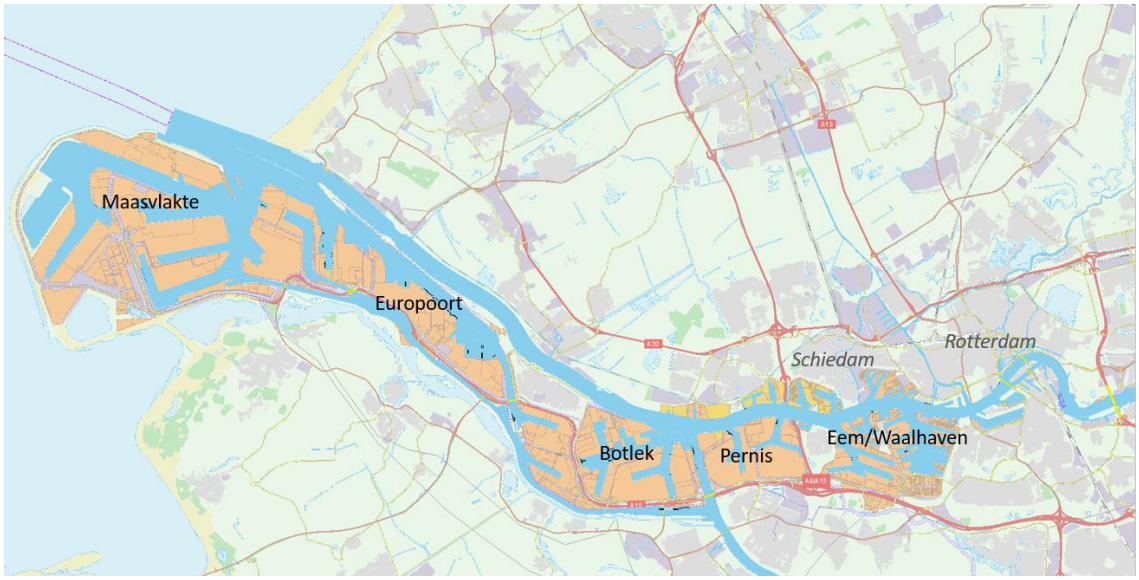


Figure 1.1: Main areas in the Port of Rotterdam, adjusted from (Port of Rotterdam, 2021)

The expansion of the port of Rotterdam in the 1960s resulted in the creation of the Maasvlakte (MV), Europort (EP) and Botlek area (BO), whereas later constructions in the period 2008-2012 shaped the current port area in the MV harbor (Koppenol, 2016). Due to this expansion, it is nowadays possible that the largest container ships with a draught of up to 22 m can navigate in the area of Europort (Rotterdam Port Authority & International Harbor Masters Association, 2021). Terminals and distribution centers are accommodated in these areas together with 40 petrochemical companies (ECSPP, 2021) .

Sediment origin and accumulation

Fluid mud and suspended sediment are present in the water body of Port of Rotterdam. The former layer is found at the bottom of some channels and harbors whereas the latter is found across the whole water column.

Based on the origin of the particles, sediment is classified as fluvial or marine sediment. The source of fluvial sediment is the two rivers on the east side of the port of Rotterdam, river Maas and Rhine, whereas the marine sediment originates from the North Sea (Kirichek et al., 2018). Thus, fluvial sediment is mainly present in the upstream port area, close to the city of Rotterdam and the downstream area in the west side contains mainly material of marine origin. The sediment particles have a density higher than water and they tend to sink and accumulate in areas with slowly moving water. Especially in smaller berths and canals, they can form mud deposits or under the correct hydrodynamic conditions, fluid mud. As a result, dredging is required in many areas of the port to maintain the desired draught for ship navigation.

Additionally, due to the tidal effect that is present in the area, the speed of the surface water varies from location to location and periodically reaches 0 m/s as the water changes form one direction to the opposite. This reduced speed of water movement allows the sediment particles to settle down and thus they accumulate on the bottom of the channel.

The periodic change in the speed can be observed in real time via the “Weather & Tide” app from port of Rotterdam. For example, the surface water speed that is recorded in Botlek on a specific day, varied from -1 to +2 m/s, with an average of 0.6 m/s. as provided in the Water&Tide open software from PoR. However, the recorded speed in smaller channels is significantly lower around 0.01 -0.07m/s.

Sedimentation traps

One way to effectively remove suspended particulate matter from the prone-to-accumulation areas is with the use of a sedimentation trap (Tempel, 2019). With the correct design a sedimentation trap can result in a reduction of dredged material in the respective area. The sediment trap is a human-made deepening with a depth of 1-4m made on specific locations in the port of Rotterdam. The working principle of the sedimentation trap can be summarized in Figure 1.2.

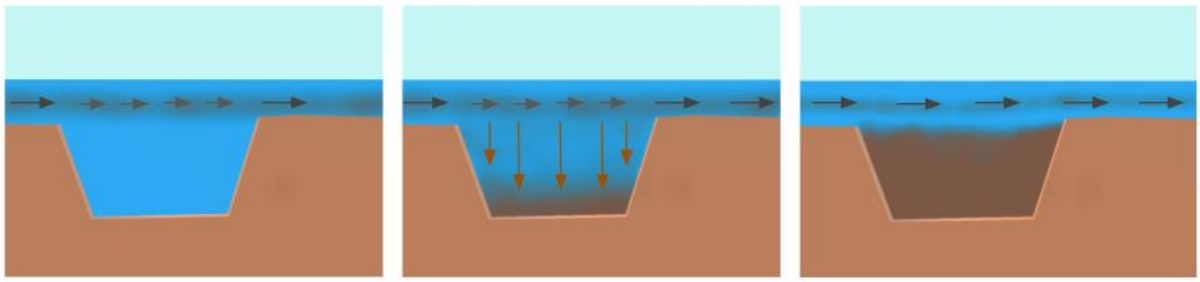


Figure 1.2: Working principle of a sedimentation trap

The difference in height between the bottom of the trap and bottom level of the channel creates specific hydrodynamic conditions that result in reduced speed of the water body above the trap. As a result, the particles start to settle and get collected inside the hole. The depth of the sedimentation trap affects its retention ability of sediment.

When the level of material in the trap is high, the trap cannot collect more sediment and there is also a risk that outflow will occur. Therefore, for the sedimentation traps to keep working they need to be frequently dredged (Y. van Leeuwen, personal communication 2021, 24 September). The dimensions of a trap can be carefully designed to ensure the best retention. The longer and deeper the trap the more sediment they can retain (Tempel, 2019).

The traps are created in locations with easy access to large capacity dredgers that can remove great volume of sediment in a short period of time. There are in total five sediment traps in Port of Rotterdam and their location can be seen in Figure 1.3. The shape of the traps can change due to the dredging operations and the conditions in the area but generally the trap can maintain roughly its original shape.

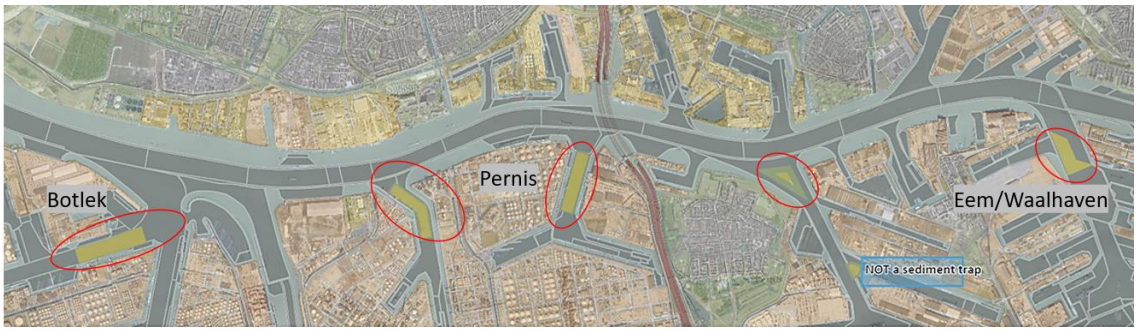


Figure 1.3: Sedimentation traps in use at PoR

Even though sediment traps can initiate the collection of sediment, they can be implemented only in specific locations in the port, where large hoppers vessels can perform dredging. In smaller channels, the access for large capacity dredgers in not possible and therefore, alternative solutions need to be found.

1.2. Project goal

This project aims to design a gel product that will help control sedimentation in the area of the Rotterdam port and as a result reduce the overall annual dredging costs. The final product should offer a solution that:

- Is applicable to the areas of attentions, ranging from easy to difficult-to dredge areas
- The dredging savings outweigh the material costs
- has low energy manufacturing and transportation requirements
- is eco-friendly
- can be repurposed at the end of its life
- contributes to circular economy

1.3. Project Scope and Approach

In this paragraph, the approach that will be followed for the product development will be presented and what falls in and outside of the project scope will be discussed. The project challenges were also identified and presented to indicate the areas where attention needs to be taken to design a successful final product.

Scope

The scope of the project is to assess both the technical and economic feasibility of various gel formulations and identify the ingredients, the manufacturing procedure and application protocol of the desired product solution. Additionally, the design will account for health and safety aspects and will be developed with respect to the environment. Consideration for the development of Kaumera will take place during the duration of the project to explore its potential. The important parameters and gel properties will also be used as inputs in the CFD stability study that is planned as a follow-up of this project. Table 1.1 gives a summary of the activities and steps that are inside and outside of scope.

Table 1.1: Scope of identifying the best gel product

	Technical feasibility	***Economic feasibility***
In Scope	• Gel recipe • Rheological behavior under shear • Stability over time • Application protocol • Parameters for CFD study	• Material cost estimation • Manufacturing cost estimation • Optimum dose • Profit from re-utilization
	Environmental considerations	**Kaumera as a gelation agent**
	• Does not pose threat to the environment and ecosystem • Biodegradable materials • CO_2 footprint • Life cycle assessment	• Relationship solids content & shear stress • Stability over time • Effect of pH • Provide development directions
Out of Scope	• Gel regeneration after destruction • Detailed economic evaluation • Extended life cycle assessment • In depth analysis of environmental impact	

Approach, challenges project planning

In the **Basis of Design Phase**, the aim is to make preliminary trials with different gelation agents to explore their possibilities and which of them can be used to create a stable gel at a low cost. The main challenge in this stage is to create a stable gel that is strong enough to keep its shape but does not obstruct ship navigation. Also, the gel barrier needs to have low cost and can be manufactured in large quantities. Simplified lab trials are planned in this phase and basic economic estimations and calculations will be used to assess the feasibility of various commercially available agents and Kaumera. The steps for the design are presented in the following paragraphs.

Preliminary trials and economic models

- Identify biodegradable gelation agents set specifications for selection
- Creation of gel products with varying content of gelation agent and solids
- Relationship between gel stiffness - shear stress
- Study the strength of gels with different type of clays and mud
- Assess stability underwater over time
- Effect of salinity on gel samples similar to existing conditions in PoR
- Concept ideas of gel products applicable in the PoR
- Model for estimation of dredging reduction costs
- Gel product target volume and material cost estimation

In the **Intermediate Phase,** the best candidates for gelation that were identified will be used to create series of gels with increasing solid mud content. The results of this study can serve as the inputs for the upcoming simulations that will determine if the gel barrier can stay in place. The challenge is the tradeoff between biodegradability and stability over time.

Main experiments and application selection

- Systematic Yield stress study for gels with selected gelation agents and increasing content of mud
- Rotating wheel experiments to investigate gel stability with movement
- Water tank experiments to visually study the gel- SPM interactions
- Define base recipe for upcoming trials
- Define the input parameters for the CFD study
- Concept ideas for application strategy, specifications

In the **Final Phase**, fine tuning of the design will take place to ensure that the proposed solution can be safely implemented. A protocol and roadmap for future development will be provided. Additionally, an assessment of the environmental impact of that the gel product will be conducted.

Fine-tuning and environmental footprint

- Results of long-term underwater study
- Additional data for CFD study (density, erosion)
- Estimation of CO_2 footprint
- Repurposing strategy at the end-of life

1.4. Project organization

Design and steering team

In this project, a consortium is formed to create a new product concept that could offer a solution to the existing problem in port of Rotterdam. The team members are actively participating by supervising, coaching, or offering advice based on their expertise (Table 1.2). The main experiments will take place in the particle size lab, located in the Deltares facilities.

Table 1.2: Steering team and areas of expertise related to the project

Company	Expertise	Supervisor/ Advisor/ Coach
Deltares	Mud properties & Rheology, CFD modelling	Lynyrd de Wit
Port of Rotterdam	Dredging operations, ship navigation, conditions on site	Yorian van Leeuwen (and team)
Rijkswaterstaat	Hydraulic engineering, Morphology, Dredging, (Water management, Regulations)	Roeland Lievens (and team)
Royal HaskoningDHV	Kaumera, Flocculants for sludge	Véronique Renard
TU Delft	Design approach, Flocculation, Rheology, Clay particles, Gel creation	Claire Chassagne (in CiTG) Alex Kirichek (in CiTG) Peter Daudey (in PDEng)

Milestones and deliverables

The project milestones are important moments in the project timeline when the team evaluates the acquired knowledge and results to take key decisions. The kick -off meeting is the first point of this timeline where a clear goal and the main objectives are defined. The project consists of three phases (BOD, Intermediate and Final) where the various targets and activities need to be executed as presented in the previous paragraph (1.4). At the end of each phase a presentation and a discussion involving the steering team will take place to assess the progression of the project. Additionally, a written report will be provided after each milestone meeting. At the end of the project the trainee will present the final design in a public colloquium considering any confidentiality restrictions.

Report structure

This report will include first a quick summary of the methodology used to come to the design of the final product. Key literature findings and explanation of models used in estimations will also be discussed before proceeding to translating the needs of the stakeholders into measurable product specifications. The product has been divided in subsystems to simplify this process. Then various concept ideas are presented for the selection of a gelation agent, product structure and application strategy. The main results are presented for the technical and economic feasibility of the gel product. Environmental considerations in terms for CO2 emissions are finally discussed. The last chapter refers to the Kaumera investigation trials to assist in the future development for the product. The main conclusions and recommendations are the last part of the main body. Some supporting information are provided in the Appendix.

Chapter 2: Design Methods

2.1. Design type and driver

This project aims to develop a new type of product that has not been previously applied in port facilities. Even though, polymeric gelation agents and clay particles have been used to improve the viscosity of drilling fluids (Akpan et al., 2020), the idea of constructing a product to control the sedimentation in large water bodies and large port areas has not been previously explored.

This project idea will be applied in the Rotterdam port area, where two existing companies, PoR and RWS, are interested in investing into a new product to reduce sedimentation in specific locations. Therefore, the approach to construct the gel is based on the current conditions and sediment flow that can be found in this specific port in the Netherlands. There is an existing market of port facilities that face similar sedimentation issues. However, the conditions vary from location to location and therefore the solution might not be applicable to ports in other countries. The developed product, its working principle and application method will need to be reassessed before proposing this solution to other port facilities.

2.2. Design methodology

For this conceptual design of a new gel product specific methodology was followed along the project. The steps are based on the Design methodology that is suggested in the Product & Process design book by (Harmsen et al., 2018). The main design levels that were utilized in this project are focused on the product design and do not yet refer to the Process technology and engineering that is required to manufacture the new product.

There are two design levels that have been implemented in the Basis of Design phase of this project, the “Framing” and the product levels of the “Supply chain imbedding”. The schemes in Figure 2.1 show what are the design steps that are applied in each design level.

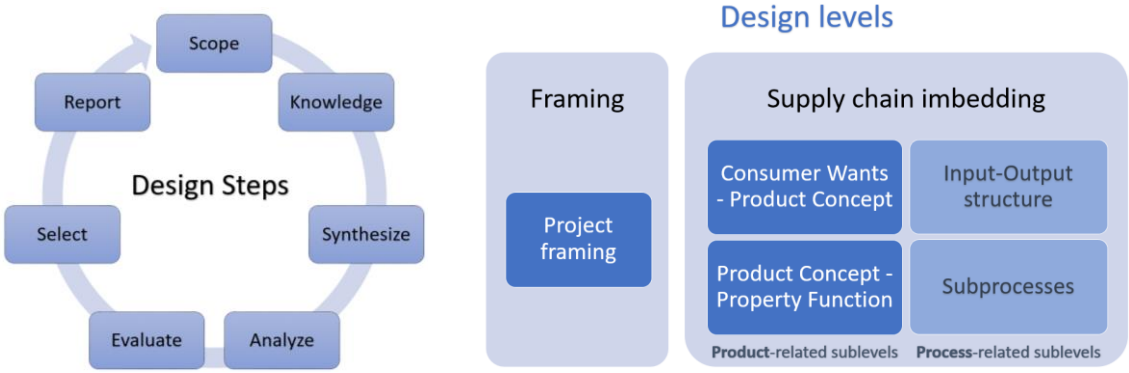


Figure 2.1: Design steps and Product Design levels from (Harmsen et al., 2018).

The main tasks that have been performed in the design are the following:

- Project framing
- Mapping of stakeholders that that can influence the design or will be affected by the design.
- Identifying the real needs of all involved stakeholders
- Translating the needs into quantifiable requirements
- Defining clear product specifications based on the requirements

Additionally, the product has been divided in sub-systems when applicable to simplify the problem. The identified components are:

- The physical appearance of the gel structure
- The gelation agent to be used in the final product
- The application strategy of the final product on site

Chapter 3: Design Presumptions & Literature

3.1. Gel definition

A gel is a viscoelastic material than behaves partially as an elastic solid and partially as a viscous liquid and contains a microscopic network in which its solvent is entrapped (Tadros, 2013). Gels can have very different characteristics and can be divided into many categories. The main ones have been described by Tadros (2013) and are presented in Table 3.1

Table 3.1: Summary of gel categories from (Tadros, 2013)

Type of gels	Characteristics of network
Polymer gels	Macromolecules - Polymer coil overlap
Particulate gels	Particle stabilization due to repulsion and Van der waals
Aqueous clay gels	Subcategory of particulate gels with dispersed thin clay platelets that sometimes can swell
Combination of polymer chains and solids	High MW chains entangled with embedded particles Mechanisms: depletion flocculation or bridging

3.2. Rheology

In this project rheological measurements are performed to characterize gels and mixtures and compare their strength and viscosity under shear. These data can be used as initial parameters for the CFD study to further assess the stability of the product. This paragraph gives a quick summary on rheology and the protocols that were used.

The science of rheology studies the way materials flow and deform. For Newtonian fluids the shear stress (σ) is proportional to the shear rate ($\dot{\gamma}$) that is applied to the material, based on the following equation,

$$\sigma = \eta \cdot \dot{\gamma}$$

where: η is the viscosity of the material

However, there are materials for which this relationship is not linear, as the viscosity changes with the applied shear rate. These are called non-Newtonian fluids. The materials whose viscosity decreases with increasing shear rate are called shear-thinning, whereas when the viscosity increases with the applied shear the material is called shear-thickening (Dilant). The typical behavior of such viscoelastic materials can be found in Figure 3.1. (Willenbacher & Georgieva, 2013).

During this project the rheological measurements were performed based on the protocols followed by (Shakeel et al., 2021) with measurements made with different geometries. For the parallel plate geometry (P35 ti L S, d=35.010mm), a gap of 2mm was utilized.

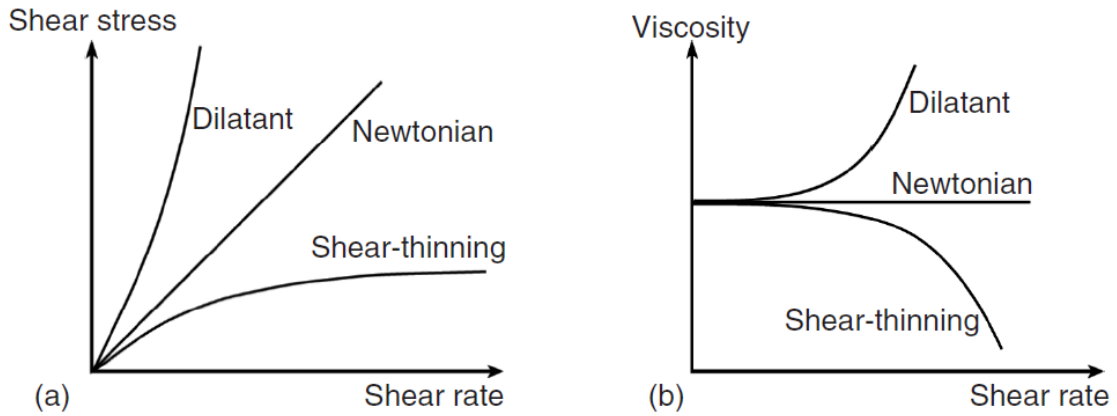


Figure 3.1: Relationship of a) shear stress and b) viscosity with shear rate for Newtonian, shear thinning and thickening materials, from (Willenbacher & Georgieva, 2013)

3.3. End-of-waste framework

A framework and specific criteria are in place to define when a product ceases to be a waste and can be utilized again as a new product. The article 6 (1) and (2) of the Waste Framework Directive defines that a product can be reused when the following criteria apply:

- The material is commonly used
- There is market demand for this material
- The material is lawful and thus it meets the existing legislation
- It does not negatively impact humans or the environment

In this project, the above framework can be enforced for the dredged sediment that would normally be rejected in the sea. As all the above criteria are met, mud from port of Rotterdam can be considered a safe raw material to be used as an ingredient in the gel barrier.

3.4. What is Kaumera?

Kaumera is a biopolymer which is produced from aerobic granular sludge originated from the Nereda® wastewater treatment process. Kaumera can be used as a bio-based alternative for which nowadays a variety of petrochemical resources is used. These gel-forming exopolysaccharides can be of value in agricultural and industrial production processes, such as bio stimulant, fertilizer coating, flame retardant or in combination with other compounds suitable for composite material.

There are two facilities in the Netherlands that are producing Kaumera, one in Zutphen with a capacity of 350tn/y and one located in Epe with annual capacity of 50 tn (Renard, V, 2021, personal communication, September 17). There are two facilities in the Netherlands that are producing Kaumera, one in Zutphen with a capacity of 350tn/y and one located in Epe with annual capacity of 50 tn (Renard, V, 2021, personal communication, September 17).

Many parties have been collaborating to commercialize Kaumera in large scale and explore new market opportunities. A list of the partners that contribute to the development of Kaumera is available in Table 3.2.

Table 3.2: Partners involved in development of Kaumera

Kaumera collaboration parties	
Waterschap Rijn en IJssel	STOWA
Waterschap Vallei en Veluwe	ChainCraft
Delft University of Technology	Energie en Grondstoffen Fabriek
Royal HaskoningDHV	EU Life Programma

Composition of Kaumera

Kaumera is available in the form of a suspension, containing approximately 7% w/w solids. The suspension contains both organic and inorganic compounds. The organic content of Kaumera is typically around 70% and consists mainly of proteins and polysaccharides. Some of the polysaccharides are neutral whereas others contain carboxyl groups. Sulfate groups are also present. The remaining 30% of the Kaumera mixture includes inorganic matter, mainly salts of K, Na, Ca, Mg or Fe (Stowa, 2019). Because of the negatively charged polysaccharides the overall Kaumera mixture also has a negative charge. The composition of Kaumera can be summarized in Figure 3.2.

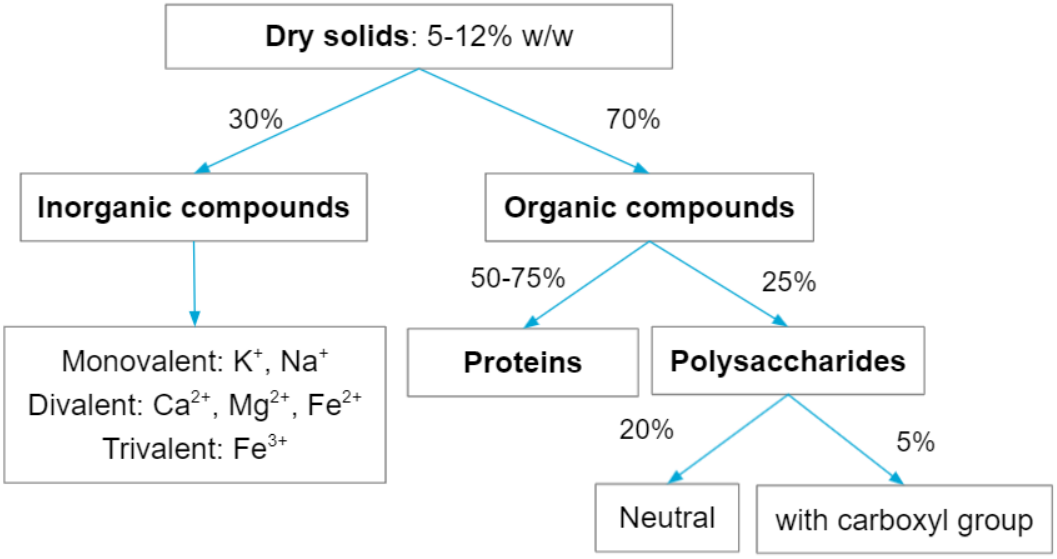


Figure 3.2: Composition of Kaumera based on (Stowa, 2019)

Mucin structure and Kaumera

Mucin is a protein that contains carboxyl and sulfate groups, and therefore in the presence of Ca^{2+} ions its polymer chains can be densely packed. Kaumera contains also similar functional groups on the polysaccharide chains and therefore is expected to exhibit similar behavior with mucin when calcium cations are available. In Figure 3.3 it is schematically presented how mucin change structure when bound to Ca^{2+}.

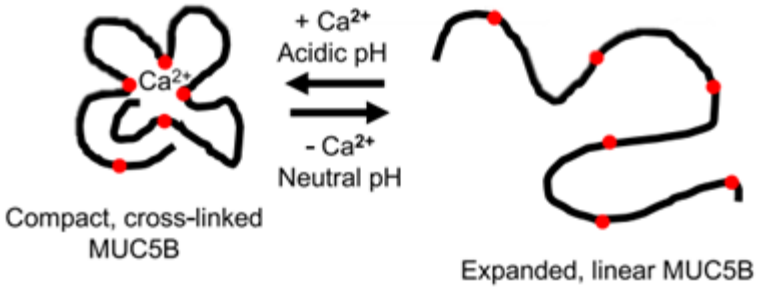


Figure 3.3: Effect of Ca^{2+} on Mucin , adjusted from (Hughes et al., 2019)

Many proteins selectively bound to calcium and not to other divalent cations like Mg^{2+}. Jing et al give the explanation that selectivity is higher towards the calcium ions because of the many-body polarization effect (Jing et al., 2018). According to this effect, it is energetically more favorable to densely pack structures around the calcium ion than other metal ions like Mg^{2+}.

Production process of Kaumera

Kaumera is produced through a combined alkalization and acidification process of waste aerobic granular sludge. In Figure 3.4 the process is presented in the respective steps.

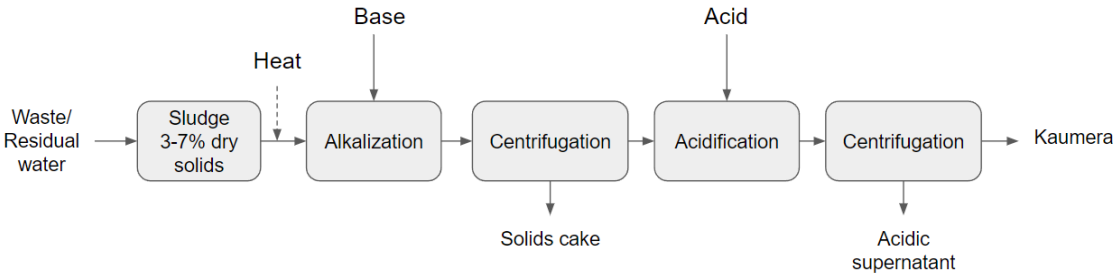


Figure 3.4: Production of Kaumera adjusted from (Stowa, 2019)

The aerobic granular sludge is a precursor of Kaumera. The sludge is a matrix of bacteria and enzymes that they produced, as well as cell debris and other byproducts. During the treatment with basic solution, most of the living bacteria are removed, even though spores might remain in the mixture. At high pH, the polymer chains extend and solubilize, whereas at acidic conditions they form a packed structure. The final and most challenging step includes the centrifugation of the mixture to separate the excess water. Depending on the content of neutral polysaccharides in the feed, the amount of polysaccharides that is suspended in the final mixture can vary. This variation influences the centrifugation step, as the neutral polymers are

solubilized and removed in previous stages whereas the charged sugars will remain in the Kaumera.

The molecular weight of the polysaccharides can vary from 5KDa to 1.5MDa. The polydispersity of sugars makes it difficult to separate then from the proteins in the Kaumera mixture. Centrifugation at very high speed at lab scale, can lead to separation in 2 phases, with the supernatant to contain a fraction rich in polysaccharides.

During evaporation of the Kaumera suspension the hydrochloric acid content is increased. When the HCL concentration become high enough, it can break down the polymer chains in smaller pieces. In this way, some groups that are responsible for flocculation become readily available. As a result, bigger flocs can be created with burnt Kaumera (at 105°C overnight) when compared to the Kaumera suspension that is not treated.

3.5. Model for Savings estimation

One of the main goals of this project is to design a product that will contribute to the overall reduction of costs in the port of Rotterdam. To estimate how much money can be saved each year a model was drafted as presented in Figure 3.5. This simplified block diagram summarizes that the spared amount of money per year is equal to the annual savings that can be achieved with the new gel product after subtracting the annual material, manufacturing cost and placement cost. The transportation cost as well as the cost of cleaning the barrier at the end of life have also been taken into account and subtracted from the annual savings.

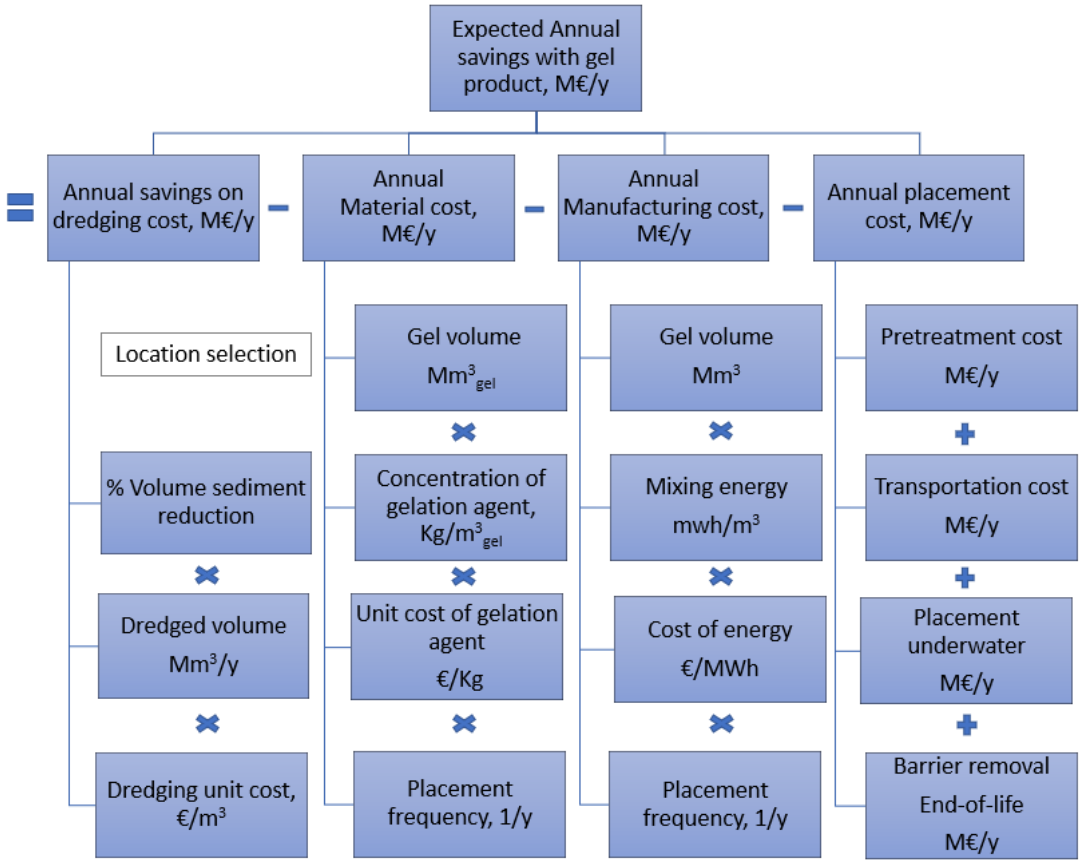


Figure 3.5: Schematic model for savings calculation

Dredged volumes of sediment in PoR

The first step to estimate the overall saving per year is to calculate how much dredged material is currently being collected from the individual areas in the port of Rotterdam. As presented in chapter 1, the port is divided in 5 main regions: the Maasvlakte (MV), Europort (EP), Botlek (BO), Pernis (PN) and Eem-waalhaven (EW). According to (Kirichek et al., 2018), the largest dredging volumes of sediment are accumulated in MV and EP areas and consist more than half of the total dredged volume. The distribution of the collected sediment volumes per area is presented in Figure 3.6.

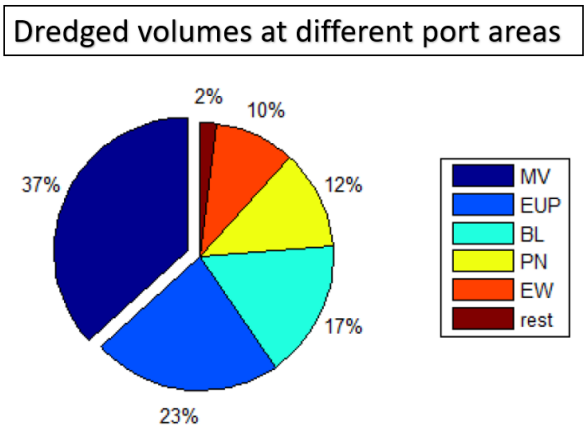


Figure 3.6: Distribution of dredged volumes in PoR per location, adjusted from (Kirichek et al., 2018)

The volume of sediment that is annually removed from the Botlek area was estimated to be between 1.5-3 Mm^3 (El Hamdi, 2012). Based on this range and the information provided in Figure 3.6, it was estimated that the total dredged volume in the port of Rotterdam varies between 8.8 and 17.6 Mm^3 each year. This range is in line with the data reported in literature by (Kirichek et al., 2018) where the volume estimation is 12-15 Mm^3/y.

Based on personal communication with the team from Port of Rotterdam, the main dredging activities in each location were identified, including dredging in terminals, in sedimentation traps, dry docks and in the access channel. This way the unit cost can be applied to each activity and the total cost of dredging can be estimated. The exact unit costs are not presented due to confidentiality issues.

Cost of dredging per area

The second step includes the calculation of the dredging cost in each area which depends on the unit cost of dredging in the region. There are many factors that affect the cost of dredging operations. The main ones were identified based on personal communication with Y. van Leeuwen, 2021, 29th September.

- Shipping distance between collection point of sediment and release point
- Difficulty of dredging in the area
- Type of vessel used for dredging and loading capacity

Types of Dredging Vessels

There are 4 main type of vessels that are used for dredging in various locations in Port of Rotterdam, as it can be seen in Figure 3.7.

1) Trailing suction hopper dredger: This type of dredger is a large vessel that can transport the collected sediment for long distances. The accumulated sediment is being collected by applying vacuum through a piping system that can reach the bottom of the channel. A pump is used to pick up the sediment and a combination of pumps can be used to collect materials from deeper areas. The hopper can release its load in specific locations in the open sea or it can be used to deposit sand close to the shore for reconstruction purposes.

A new hopper dredger with a capacity of 5,500 m^3 started to operate in the area of the Rotterdam port in 2019 (DredgingToday, 2019). The vessel is named Ecodelta and is owned by the van der Kamp contractor. The large size of the ship enables it to dredge quickly big volumes of sediment. According to an email discussion around 3,500-6,000 m^3 can be collected with a hopper vessel in 3-4 hours (A. van Hassent, personal communication, 2021, 12th July). Hence, the average collection rate with this type of dredger can be estimated to be around 20 m^3/min. As a difficult to maneuver vessel it cannot access smaller areas in the port, and thus it is used to dredge easy to reach areas, like sediment traps.

2) Backhoe Dredger: This type of vessel can grab sedimented matter and sand and transfer it to a nearby location, for example into a sedimentation trap. The small size of the vessel gives it the ability to remove sediment from small channels and less accessible locations. Some vessels of this type can dredge as close as 30cm from the terminal (Leeuwen, Y., 2021, personal communication, September 29). The typical volume of material that is deposited in a sediment trap per cycle is 500-900m^3 and the frequency is once or a few times a day. (A. van Hassent, 2021, Personal communication, 12th July).

3) Cutter suction dredger: The vessel is being used to remove high density material, including rocks and sand. The dredger works by setting a vertical pole on the channel's bottom that serves as the rotational axis for its cutter. The cutter then scrapes the sedimented hard material by swinging from side to side while with suction it can pick up the debris created. Once the area is clear, the vessel moves its axis pole further away and repeats the process (Leeuwen, Y., 2021, personal communication, September 29).

4) Water injection Dredger: Unlike the previously presented types, this dredger does not pick up the material. Its function is to dilute mud laying on the bed and turning it into a turbidity current by applying a high volume, low pressure stream of water. The suspended particles with this method can freely move by the water current and naturally be collected into a sedimentation trap (Kirichek & Rutgers, 2020). WID is suitable to be used in less accessible areas.



Figure 3.7: Type of dredging vessels commonly used from (DEME, 2021), (Van Oord, 2019)

With respect to the difficulty of dredging, areas that are closer to the sea can be reached by large vessel like the Ecodelta. On the other side, the confined regions close to terminals and in narrow channels need to be dredged with smaller ships, like the backhoe dredgers. The latter usually need more time than the hoppers to pick up a specific volume of sediment and therefore they are most costly to operate per volume. Finally, in the areas that are not accessible by neither of the above types, because of limited space, Water Injection Dredging (WID) is the solution. Because of the difficult accessibility of the latter areas the dredging costs are higher in these locations.

Considering all three factors, the distance to the sea, the type of dredger required and the difficulty to dredge the area, an estimation was made for the unit costs of dredging in different areas in the port. In this report only the actual dredging costs per area are not presented to protect confidential information.

Chapter 4: Product specifications

Setting product specifications on an early stage in the project can assist product development as it gives a clear way on how to evaluate various concept ideas and select the most promising one. Based on the methodology that was presented in Chapter 2, the needs of the stakeholders are initially translated into quantifiable requirements and finally into product specifications.

4.1. Stakeholders

Both internal and external stakeholders play an important role in the design of the final product. The list of internal stakeholders includes the steering committee and was presented in chapter 2. The main categories of people and companies that are affected by the design or can contribute to the development process are presented in Table 4.1.

Table 4.1: External stakeholders

External stakeholders	
Are affected by the design	**Can influence the design**
Port and Terminal operators	Water treatment companies
Dredging companies	Environmental regulatory affairs
Marine contractors	

4.2. Identified Needs

The needs of the various stakeholders were identified based on literature research and discussions with the member of the steering team. Once a list of all the desired features and functions was created, the needs were grouped into main categories as shown in Table 4.2.

Table 4.2: Needs categorized into groups

Identified needs	Main groups of needs
● Reduce overall dredging procedures ● Reduce dredging in difficult areas	**Less dredging**
● Ships navigate safely above & through the gel ● The gel keeps its shape for desired period	**Stable gel**
● Use of cheap raw materials ● Low energy for manufacturing	**Low cost**
● Biodegradable raw materials ● Low CO_2 footprint ● Repurposing strategy ● Contributes to circular economy	**Eco-friendly product**
● Easy onsite preparation ● Easy dispersion and mixing ● Gel can be deposited with existing vessels	**Easy preparation**

4.3. Quantifiable Requirements

After grouping the needs into classes, it is easier to set the requirements and their target values for the gel product. Each requirement is presented in Table 4.3 and is associated with a specific group of needs. The acceptable ranges of the properties and the selected values were estimated from literature search, communication with team experts or based on the models that were presented in chapter 3. A detailed explanation is provided in Appendix C.

Table 4.3: Translation of needs into measurable requirements

Need	Requirement	Metric	Range	Target
Less dredging	Reduction of dredging operation	%/y	5-30	10
	Reduction of dredging cost	M€/y	0.75- 4.5	1.8
Stable gel	Gel placement frequency	Batch/y	0.1-10	<3
	State of gel	NA	Liquid - stiff	Per application
Low cost	Material cost	€/m^3	10-200	20
	Manufacturing cost	€/m^3	0.1-2.0	<0.5
	Application cost	€/m^3	0.5-2.0	<1.0
Eco-friendly	Biodegradability	%	90-100%	100%

4.4. Product Specifications

In the final step the requirements that were previously presented are shaped into product specifications. Because of the complexity of the product, the specifications are split into three sub-systems; 1) the gel structure of the product, 2) the gelation agent to be used and 3) the onsite application strategy and 4) the technique for applying the product underwater.

The main needs that the application approach needs to include refer to the time, cost and availability for manufacturing, transferring, and applying the product on site. Firstly, translation of these needs will provide the specifications that the overall strategy needs to fulfill. Secondly, a closer look will be given to the unloading method that can be used to deposit the barrier on site. The specifications that were set for this discharging technique are broader and can potentially be considered for application of other gel structures, such as liquid gels and flocculation agents.

4.4.1. Specifications for Product Gel structure

The first sub-category refers to the structure of the final gel product, the shape and its appearance when placed underwater. A list of the specifications for the gel product and its structure are shown in Table 4.4.

Table 4.4: Specifications for a gel product

Requirement	Specification	Metric	Range	Target
Reduction on dredging operations	Volume of sediment reduced due to product	Mm^3/y	0.75 - 4.5	1.5
Placement frequency	Lifetime of gel	years	0.1-10	<1
Gel stiffness	Yield stress	Pa	50-500	Per application
Salinity	Concentration of salt in the final gel	%w/w	0.1-3.5	<2.5
Material cost	Concentration of gel agent Unit cost of gel agent	%w/w €/kg	0-5 0.5-20	1 <5
Manufacturing cost	Energy required for manufacturing	GWh/y	0.5-33	<10
Biodegradability	Degradation rate	% Weight loss/ y	1-100%	>50

4.4.2. Specifications for Gelation agent

The second sub-system is related to the use of the main gelation ingredient. The Table 4.5 presents the list of specifications for gelation agents and target values to build a stable gel network, in big quantities and at low cost. Further explanation is provided in Appendix A1.

Table 4.5: Specifications and targets for gelation ingredient

Requirement	Specification	Metric	Range	Target
Gelation	Concentration*	%w/w	0.1-10	<5
Gelation	Time	Min	1 - 300	<5
Dissolution	Temperature	^oC	5-20	10
Stability underwater	Time	weeks	1-24	>6
Gel strength	Yield stress	Pa	50-300	100
Mixing energy	Shear	-	Low- high	Low- Medium
Gel fluidity	Viscosity at 1%ww	mPa.s	2- 3,000	>1,000
Cost of the gel	Material cost**	$€/m^3_{\text{of gel}}$	20-200	25

* % mass of dry gelation agent in total mass of the final product.
** Manufacturing and deposition costs were not considered during the gel agent selection.

4.4.3. Specifications for application strategy

The last sub-system is related to the application of the final gel barrier in the Rotterdam port area. The application strategy needs to include a method for:

- preparing the gel barrier or premixtures necessary for its production,
- transporting the gel and materials involved to the desired location and
- unloading the final gel barrier on site.

A base case was defined to be able to set target values for the gel barrier concept. This refers to manufacturing and placing a 5,500 m^3 gel barrier in the Botlek area of Rotterdam port. The details and assumptions made for the base case can be found in Appendix A6. The Table 4.6 presents the list of specifications that the application needs to fulfill. The use of more than one pumps in parallel is suggested for mixing the barrier, thus mixing time can be achieved in <1h.

Table 4.6: **Specifications** and targets for application method of **5,500m^3 gel barrier**.

Requirement	Specification	Metric	Range	Target
Fast application	Pretreatment time	h/barrier	0.1-4.0	2
	Mixing time		0.4-2.4	<1
	Transportation time		0.5-3.0	1
	Placement time		0.9-2.0	1
Low cost	Pretreatment cost (polymer)	€/barrier	1-150	50
	Mixing cost		50-500	150
	Transportation cost		10-1000	500
	Unloading cost		100-500	250
Applied by existing personnel	Level of expertise required	-	Low-medium	low

4.4.4. Specifications for unloading method

Focusing specifically on the unloading technique a set of specifications were made to assess the performance of various discharging techniques. The Table 4.7 provides specifications for discharging applicable to every structure, from dense to liquid-like gels.

Table 4.7: Characteristics of the unloading method used for deposition

Requirement	Specification	Metric	Range	Target
Fast discharging	Unloading capacity	m^3/h	500-6,000	5,500
Operation cost	Cost of unloading	€/m^3	0.02-1.2	0.5
Availability on site	Equipment availability Degree of training required	- -	existing – can buy Low- medium	existing low
Accuracy of placement	Radius of the circle within the product can be placed	m	0.5-50	<10

Chapter 5: Concept ideas and evaluation

During the project brainstorming sessions and discussions have been conducted with the stakeholders to generate partial ideas for the previously mentioned sub-systems of the product. By utilizing the *SCAMPER* list (**S**ubstitute, **C**ombine, **A**dapt, **M**odify, **P**ut to another use, **E**liminate and **R**everse), different ideas were combined to form complete application approach concepts. The following concepts are presented and evaluated here against the defined criteria:

- Concept ideas for possible gel structures in the port area
- Concepts for application specifically for the gel barrier idea
- Concepts for unloading on location various gel products

5.1. Gel structures in Rotterdam port area

Wirth respect to controlling the sedimentation rate in different areas in the port, a discussion with the team from Port of Rotterdam and members of the steering committee yielded six concepts that can be grouped into two categories:

1) Fluid gels products that can be contained in specific locations in the port of Rotterdam and take the shape of the cavity that they are placed.

2) Stiff- solid like gels that can maintain their shape and physically hinter the flow of incoming mud particles in targeted locations.

An overview of the concepts and their potential application point is available in Figure 5.1, whereas details on each concept are provided in the Appendix B. Additional ideas of application locations in the RWS area of the Rotterdam port are briefly presented in Appendix F.

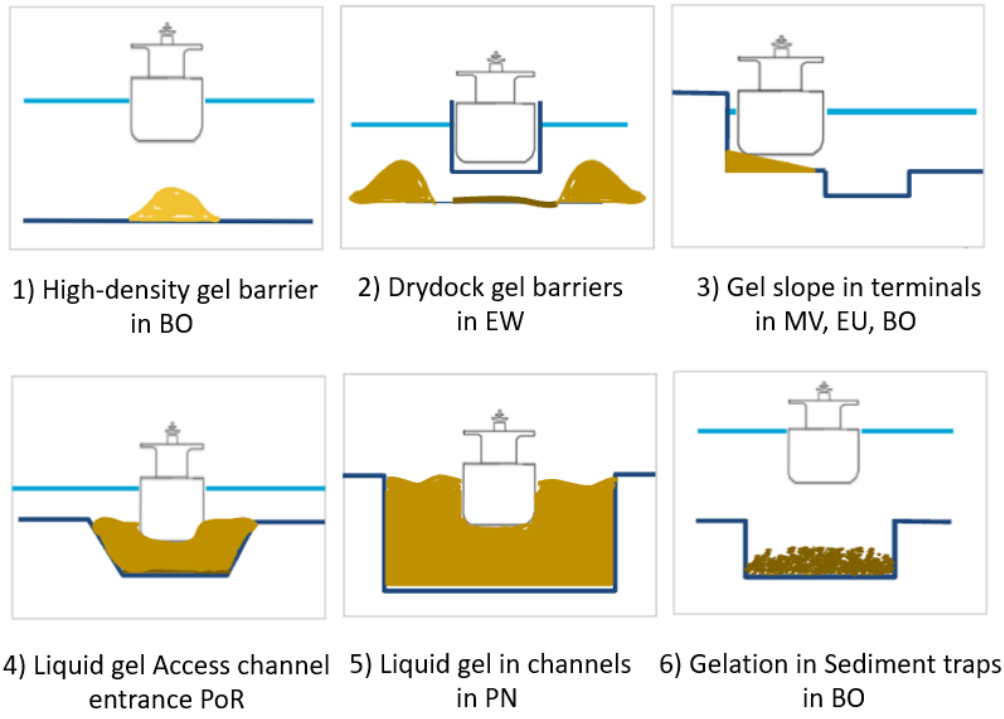


Figure 5.1: Summary of concept ideas and port area of application

The six concept ideas give different approaches on how to handle sedimentation in the port. The volume of the gel barrier in Botlek entrance and in dry docks is a key factor that will determine the performance of the barrier and the restriction of particles that can be achieved. Additionally, the barriers need to be stable for a desired period to make this solution economically feasible.

- The high-density gel idea acts as a physical barrier that can limit the spread of incoming sediment particles in specific locations in the port.
- The same principle is applied in the case of dry docks, which are maintenance locations for vessels in the port. When the dry dock is in-use (lifted), an empty area is created below it, which accumulates sediment overtime. Once the ship is ready to sail back the sediment prevents the dry dock from returning back to its original position, therefore dredging is required. Placing gel barriers around the dry dock could prevent sediment from entering the area below the dry dock and could reduce dredging costs.
- The slope barrier principle aims to reduce sedimentation from the areas that are more costly to dredge. The barrier in this case will lead the volume of sediment in easier collection areas where dredging is cheaper, like sedimentation traps. It is worth mentioning that the slope barrier will be accompanied by higher maintenance costs to preserve its shape.
- In the case of the liquid gel in the access channel, sedimentation can be prevented if the channel remains filled with the fluid gel. However, due to water currents it is expected that a portion of the gel will be carried away. In this project phase the exact quantity of the removed material was not defined and was not considered in the calculations. If this concept idea scores high enough in the comparison matrix, a more detailed estimation will take place in the upcoming project phases.
- For the liquid gel that aims to substitute the water body in small channel, the sedimentation can be prevented by 100% as the mud particles cannot enter the area. However, environmental aspects with respects to the surrounding ecosystem, should be carefully evaluated for this option.
- Finally, in the sedimentation traps the addition of the gelation agent will promote flocculation and retention. In this way, the sediment (dry equivalents of mass) that can be accumulated is increased and dredging is not required as frequently. An ecofriendly flocculant, like Kaumera, is a promising candidate to consider.
- The assumptions that were made for the estimated values can be found in Appendix B6.

The concepts were evaluated based on the requirements and specifications that were described in Chapter 4. The results of the comparison show that both fluid and stiff gels could potentially be beneficial for PoR when used at specific locations. The results are presented in Table 5.1.

Table 5.1: Evaluation Table of concept ideas

		1	2	3	4	5	6	
Specification	**Metric**							**Target**
Volume of sediment avoided	Mm^3/y	1.1	2.9	0.9	1.2	1.8	1.7	1.5
Amount spared	M€/y	1.1	5.8	5.0	0.7	4.3	2.7	1.8
Lifetime	Years	0.1	1.0	2.0	10	20	0.5	<1
Concentration gelation ag.	% w/w	1	1	1	0.5	0.5	0.5	<1

The selection of a specific concept is not possible at this stage of the project. It is worth investigating further both types of gels to acquire more knowledge about the gel properties and lifetime.

5.2 Application strategies for a gel barrier

During the intermediate phase three main application concepts were formulated with respect to the application method of the high-density gel barrier. The main ideas include the manufacturing of the following:

1. Batch preparation on a barge ship and application of the selected location
2. In-line continuous preparation and direct application on location
3. Application of a premade gel barrier mixture prepared on an industrial site

A quick overview of the concepts is presented in the Figure 5.2 below followed by a brief description of their characteristics. A more detailed explanation of each concept is presented in Appendix G.

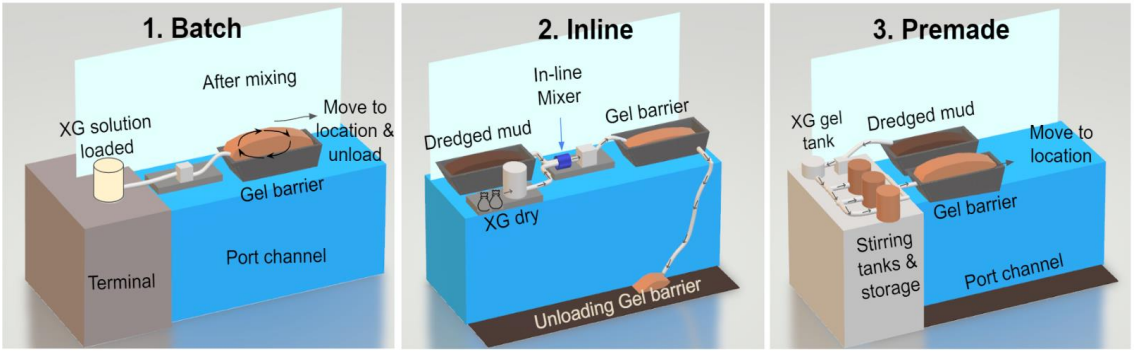


Figure 5.2: Main application concept ideas for a high-density gel barrier in Botlek area

The **batch approach** aims in manufacturing the gel barrier inside a barge vessel close to the terminal. This method utilizes a premixture of liquid polymeric solution that is mixed with dredged mud to create a barrier on the vessel. Once the gel is thoroughly mixed and

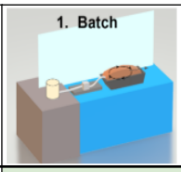
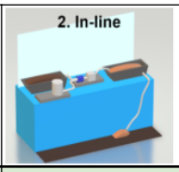
homogenized the barrier can be transferred to the target location and applied with an appropriate discharging method.

With the **in-line approach** the preparation of the gel barrier takes place on site with the use of an in-line homogenizer. Gelation agent in powder form is mixed with dredged mud through the homogenizer and the final gel barrier is formed. The procedure can take place continuously while the mud- dredging operation is still ongoing and by directly applying the final mixture on location.

The final approach that is presented, refers to preparing a gel barrier on a mixing facility near the port, transferring and applying the **premade barrier** where it is needed. Dredged mud needs to be carried to the land site, mixed with a liquid solution of gelation agent, and transported back to the channel for application.

The three concepts are compared in Table 5.2 and their performance is assessed based on the target specifications.

Table 5.2: Performance of concept application ideas for gel barrier and evaluation against specifications

Specification		**Metric**	 1. Batch	 2. In-line	 3. Premade	**Target**
Details	*Pretreatment time*	h/barrier	1.6	0.6	1.6	2.0
	Transportation time		0.8	0.6	1.4	1.0
	Mixing time		1.0	1.0	1.0	1.0
Total time		**h/barrier**	**3.6**	**2.5**	**4.3**	**4.0**
Details	*Pre-treatment cost XG*	€/barrier	21	0	100	50
	Mixing cost		59	374	263	150
	Transportation cost		870	124	1,068	500
Total Cost		**€/barrier**	**950**	**498**	**1431**	**700**
Expertise required in port		-	**medium**	**medium**	**low**	**low**

The comparison of the three ideas was made based on the same conditions, gel structure and application location. During the assessment it was concluded that the time of manufacturing and the total cost are related; The lower the overall application time, the higher the processing cost as more mixers need to be utilized to process the 5,500m^3-volume of the barrier. This relationship is not proportional and depends rather on the capacity of the equipment involved. Therefore, to achieve a fair comparison, the concepts were evaluated for the same time basis (approximately 4hours), same recipe and while using the same unloading technique. For this reason, the dredging costs are the same for all the discussed approaches and therefore are not presented in this table. Based on the estimation of dredging cost = 0.4 €/m^3, applying the barrier on locations and cleaning the barrier fragments at the end of life will add an additional cost of 3.500 €/barrier.

5.3. Unloading techniques for gel products

The technique to be used for unloading the gel barrier is an important part of the application strategy. The most appropriate technique will vary from concept to concept as liquid gels and dry powders are easier to handle in large volumes than stiff viscoelastic materials. From discussions with the steering team, it was concluded that the four methods that are available for material disposal or placement are:

1) through **a pipe**, 2) with **fascine mat**, 3) with a **grab barge** or 4) via a **barge split** hopper vessel. As an example, the four techniques are visualized in Figure 5.3 for the case of the gel barrier concept.

The following paragraph includes a quick presentation of the concepts, whereas the details of each unloading method are presented in Appendix D.

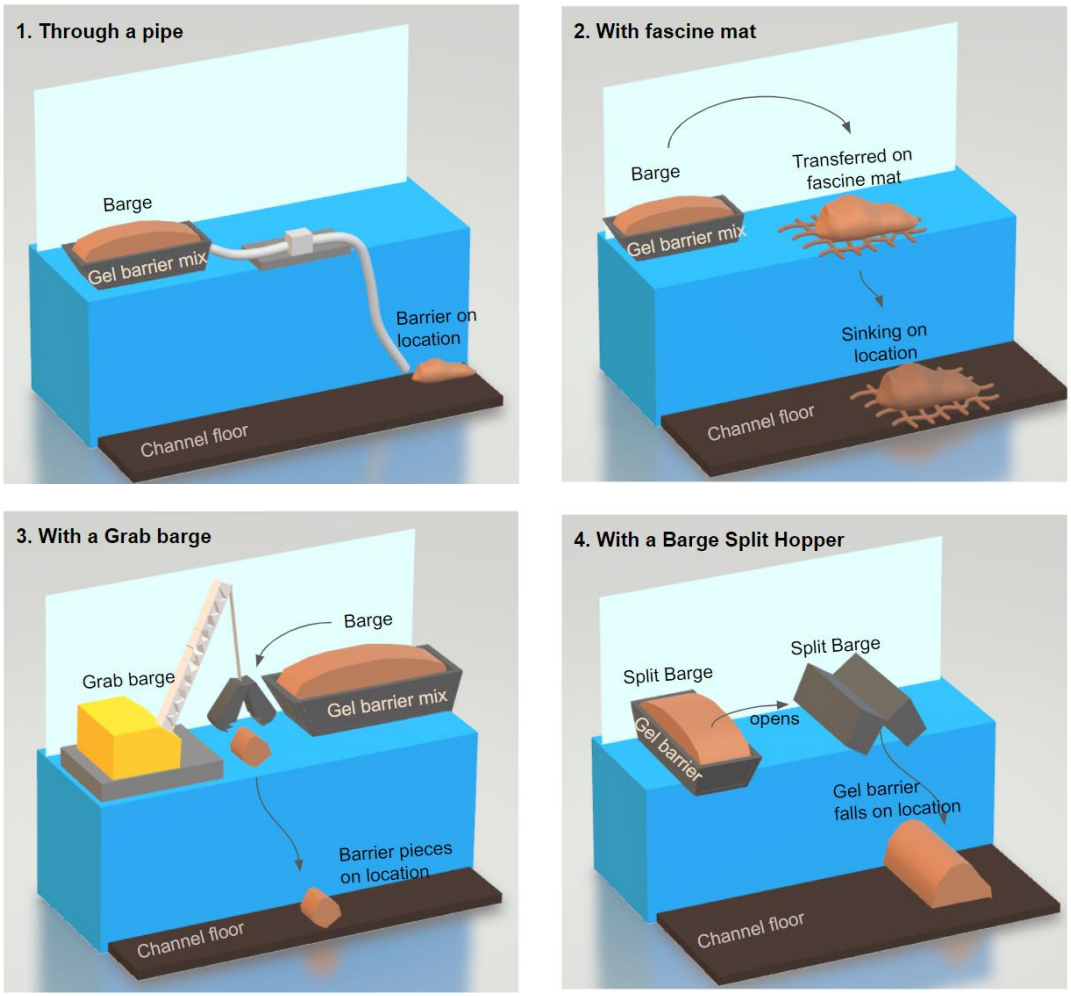


Figure 5.3: Unloading techniques for a gel barrier product in Rotterdam port area.

1) Unloading the mixture **through a pipe** is the first technique that can be used in the PoR and RWS area in the port. The final mixed gel can be placed with the use of existing equipment with good accuracy of the location of application. According to the quantity of gel that is to be deposited a series of pumps and vessels will need to be utilized.

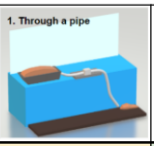
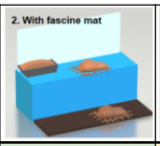
2) The second option is the sinking platform of **a fascine mattress** that can deliver the total volume of semi-solid structures directly in the desired location. Removing the mattress after use is required as the material is not suitable for navigation.

3) The application of the product with the **grab barge** in a vessel or on terminal is also presented. This suggests placing the product in smaller loads onsite. The capacity of the grab is the main factor affecting the unloading time. High precision is possible with this method.

4) The final concept is the quick disposal via a **split barge** vessel. As discussed in the BOD report this special vessel can open and deliver its load above a specific location. The accuracy of this application is lower as the product might be transferred away by currents; however, the unloading time can be very low.

After shortly presenting the available ways for unloading material in the Rotterdam port area, the four ideas are evaluated against the specifications that were set in Paragraph 4.4.4. The summary can be found on Table 5.3.

Table 5.3: Comparison matrix for unloading techniques in Rotterdam port area

Specification	**Metric**					**Target**
Unloading Capacity	m^3/h	2,000/pump	5,500	2,000	7,500	5,500
Cost of unloading	$€/m^3$	0.40	14.00*	1.12	0.03	0.50
Availability on site	-	existing	Less used	existing	existing	existing
Degree of training required	-	medium	high	high	low	low
Accuracy - Radius of application	m	<1	<10	<2	100	<10

* Based only on manufacturing cost of brush mattresses

The Table 3.2 shows a quick evaluation of the characteristics of the four unloading methods in the case of a stiff gel barrier product. Using a pipe to deposit the product can be achieved with low cost and high accuracy, whereas the capacity can be increased by utilizing multiple pumps. This application is favorable with lower gel product volumes, such as in the gel barrier and gel slope ideas. The grab barge is also a suitable technique for stiff gels when precision is required. However, the operating cost of the equipment is higher than the placement with a dredger via a pipe (Van der Meulen et al., 2020). For application on bigger areas and with large quantities of gel, accuracy is not a limiting factor, and the split barge method is preferred. The use of fascine mattress is an elaborate process, requiring more expertise from personnel. Additionally, the manufacturing cost of those mattresses is too high to in comparison to the other techniques.

Therefore, the deposition method is strongly related to the structure and stiffness of the gel that needs to be applied. For the five remaining concepts of a gel product a table was formed to quickly assess the compatibility of various mixing strategies and placement techniques in the Rotterdam port area. This can be found in Appendix E.

Chapter 6: Technical feasibility

During this project many trials took place to study the gel strength that can be achieved with varying concentration of gelation agents and solids content. The purpose of the study was to get an initial idea of the gel strength that can be achieved with commercially available gel ingredients such as xanthan gum (XG), guar gum (GG) and Carboxy Methyl Cellulose (CMC). The use of polymers, like Xanthan gum is common in offshore operations as, for example, it can be used as a rheology modifier in drilling fluids.

The technically feasibility of constructing stiff gels with Kaumera suspension was also investigated. In total 88 samples were prepared for this study and the main results and conclusions from the trials will be presented in this chapter. Supporting information about the sample preparation, the ingredients that were used and the codes of the samples can be seen in Appendix C.

6.1. Type of gels

After completion of the preliminary measurements, it was observed that three main types of gels can possibly be developed as a gel product. Liquid, Low-density, and High-density gels.

Liquid gel products: These gels can easily flow and are dispersed when placed underwater. Additionally, they start to consolidate due to gravity after storage of more than a week. This type of gels could potentially be applied in the access channel and in channel port aeras, where the shape of the gel is not an important factor.

Low-density gels: These samples resemble a solid soft mass that retain their shape. When placed underwater the gels either float immediately or flotation occurs with swelling of the gels. The low density of the product originates from the entrapped air in the formulation during manufacturing. Additionally, when swelling occurs the volume of the sample grows, and the density is further reduced. It is also speculated that dissolved air might be accumulating in the gels overtime, as the water sample is not degassed. These gels could be possible applied in different project, like for example in oil spill control.

High-density gels: These stiff gels contain a concentration of solids high enough to maintain a density heavier than water even after swelling has occurred. The samples can preserve their original shape for some time underwater, although depending on the gel stiffness, deformation and flattening of the gel might be noticed 1 to 4 weeks after the placement. The stiff gels can be used as a physical barrier that hinders or reduces the inflow of particles in a specific area of the port.

A summary of the shear stress, the appearance of the gel samples and the observed underwater behavior for all samples is shown in Figure 6.1. The exact composition of the samples is shown in Appendix C, (Table C3). The color in which the sample is marked indicates:

- Red= Liquid gels that disperse in water
- Yellow= Low-density gels that float,
- Green= High-density gels that remain underwater

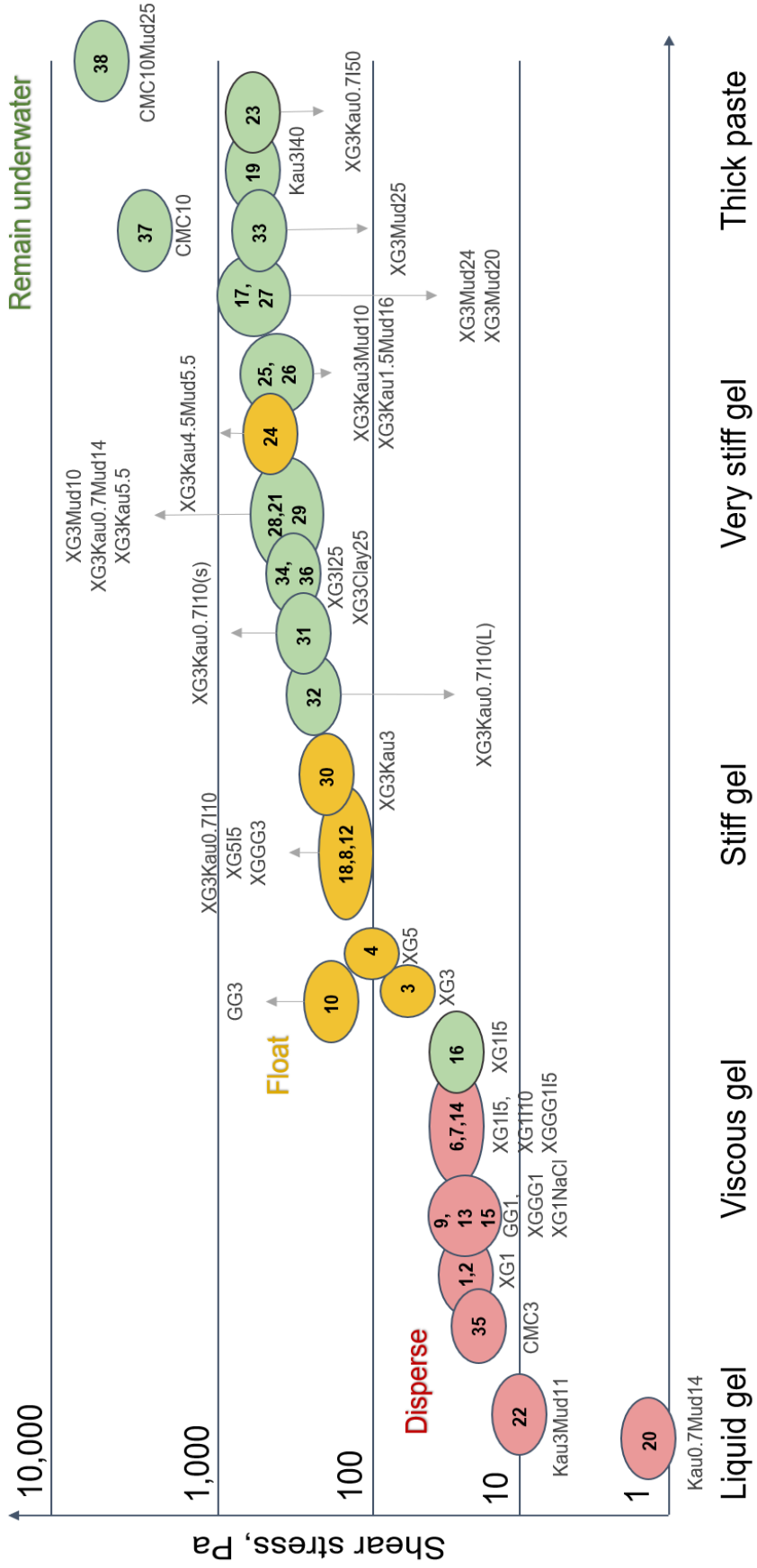


Figure 6.1: Main categories of gel samples made in preliminary phase (codes on Table C3)

6.2. Relationship shear-stress and gelation agent concentration

A systematic rheological investigation was performed to study the effect that polymer concentration and mud content play on strength and stability of the barrier.

Xanthan gum and Carboxy methyl cellulose, were the main ingredient that were studied rheologically for different added mud contents. The samples that were made contained 1% or 3% w/w XG combined with mud from port of Rotterdam with concentrations between 0 – 25% w/w. For the CMC samples, a polymer concentration of 5% was used, to achieve a gel with similar strength as XG. The solids content of the mud sample was determined with a loss-on-drying test and was 31.5%w/w. The relationship between shear stress and shear rate was measured for each sample at 20°C, the yield stress was extracted by fitting the Bingham model on the data and the summary of the results is shown in Figure 6.2.

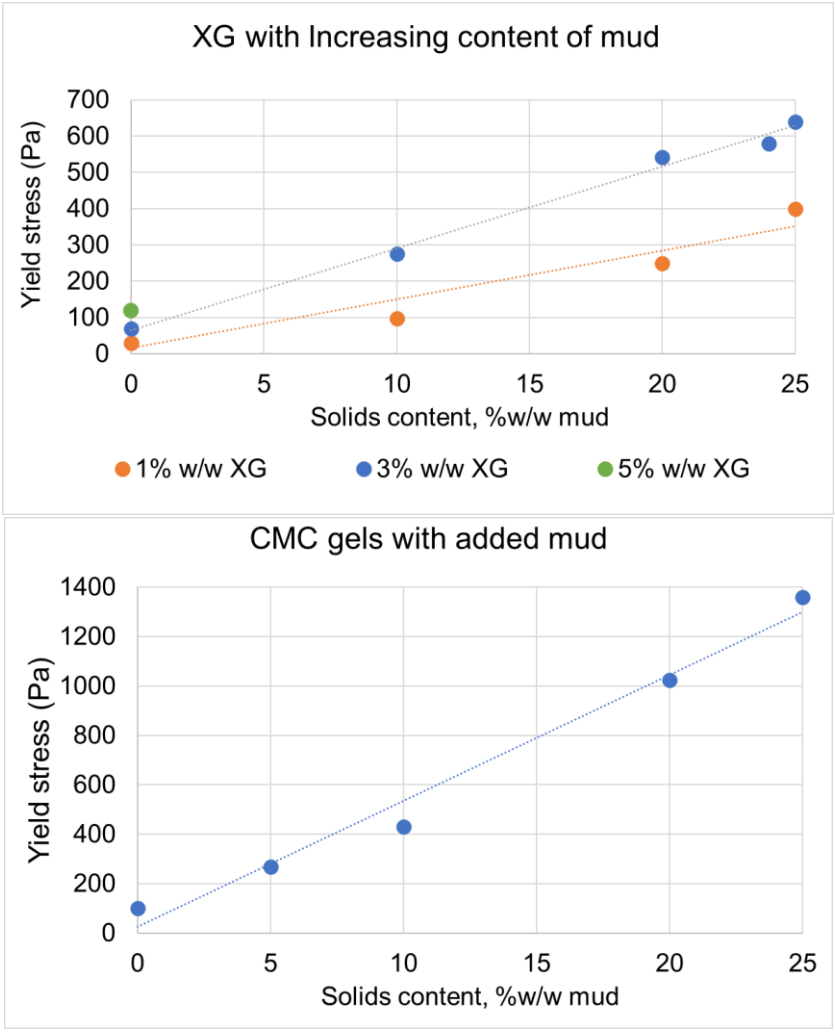


Figure 6.2: Yield stress -mud content relationship for XG gels (above) and CMC (Below)

From the graph, the yield stress with the solids content shows a linear relationship both for 1% and 3% XG concentrations. The same strength can be achieved either with 1% XG and 20% Mud or with 3% XG and 10% Mud. It is expected that a series with 0.5% XG will also exhibit similar

linear behavior and is possible that the desired stiffness of 250Pa can be achieved with the addition of higher concentration of mud (estimated around 25-30%w/w).

For the CMC series, the yield stress of the gels also has a linear trend with added solids. It also results in stronger gels (higher yields tress values) as it contains more polymer (5%of CMC instead of 1%or 3% of XG). This selection has been made for practical reasons as manufacturing CMC gels with lower polymeric content did not produce stiff gels but rather diluted suspensions.

6.3. CMC and XG stability in water

The stability the above gels (CMC, XG gel) was also evaluated with a small-scale underwater experiment. Approximately 10g of each sample were placed in a water tank containing tap water. The gels were observed over time as it can be seen in Figure 6.3. A small description of the composition is provided, whereas the samples codes are explained in Appendix C (Table C3).

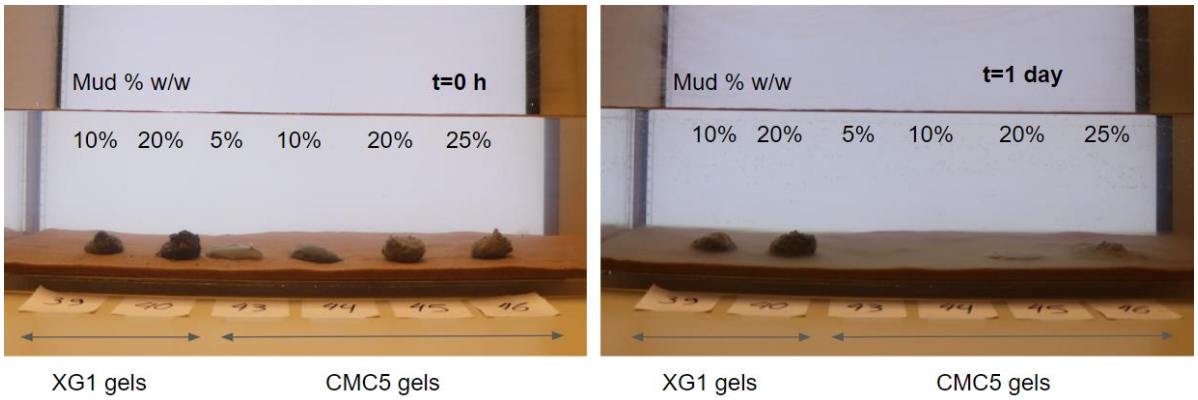


Figure 6.3: CMC and XG gels underwater (codes on Table C3)

Despite being stronger in terms of yield stress, all of the CMC gels seems to dissolve very fast when placed underwater. The gels that contain less than 10% solids dissolve in the first 3 hours underwater, whereas the stiffer gels with (1000Pa) dissolve in less than 1 day. Therefore, due to the high dissolution rate use of CMC, this gelation agent is not appropriate for building a barrier structure underwater.

6.4. Effect on salt concentration

From the preliminary trials that were performed in the initial project phase, salt might have a strengthening effect in the rheological properties of gels (Appendix C2). Based on this observation, a gel of known strength, XG1Mud10 was prepared and compared with the same gel composition but dispersed in 2.5%w/w NaCl water and 25% NaCl water respectively. After homogenization, the gels were left in the fridge for 4-9 days and then tested in the rheometer. The results are shown in Figure 6.4.

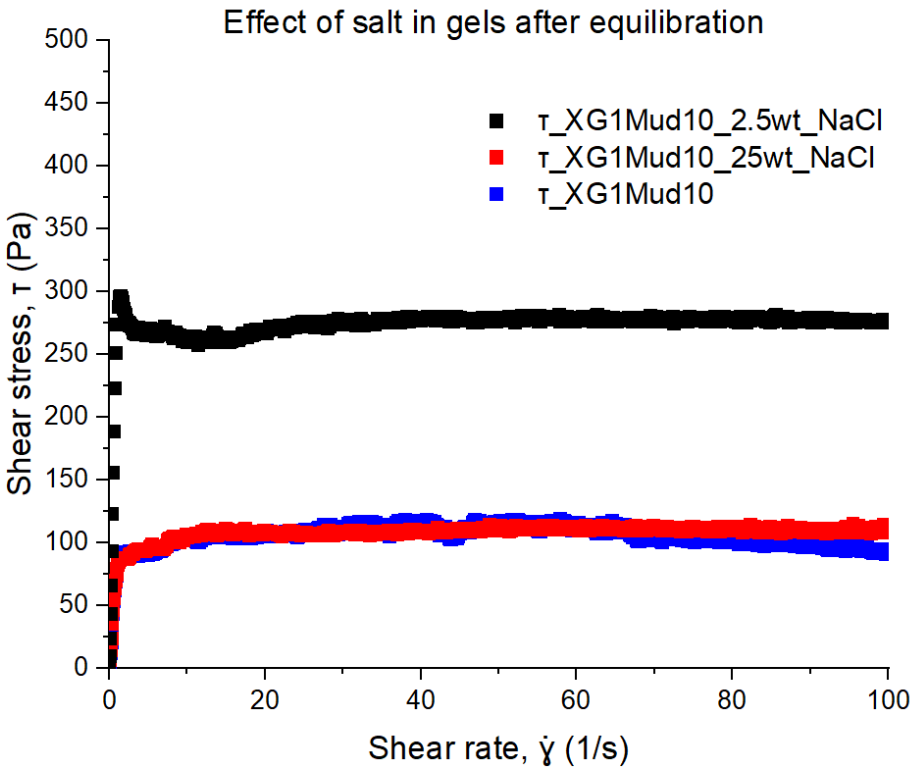


Figure 6.4: Effect of salt concentration in strength of the gels

Adding 2.5% salt in XG1Mud10 gels seems to increase the gel strength up to 3 times more than the initial gel without salt. On the contrary, for very high NaCl concentration (25%wt) the gel properties are similar to the initial XG1Mud10 gel. This suggests that there is an optimal concentration of salt the results in a stiffer gel. It is assumed that the cations of Na^+ contribute to the stability of the network by creating coils of XG with bonded clay particles. If the solution contains high salt concentration, then the charges on the polymeric chains are screened and there are no further interactions with the mud, thus no improvement in the strength of the gel.

6.5. Strength and stability of gel barrier

From observation of previous gel barrier recipes, it was concluded that xanthan gum is the gelation agent that could potentially be used in the desired application as a barrier. The gels containing xanthan gum and mud tend to swell when placed underwater as water is being absorbed by the polymeric chains. This results in an increase in the specimen volume which is also affected by the scale of the experiment. Initial experimental indications suggested that for small gel samples (10-20g) the volume increase is greater than for bigger samples (200g) after 24h. Therefore, it was decided to perform a consistent study to study the swelling rate of a 250Pa gel barrier recipe in 2.5%wt saline water.

6.5.1. Barrier volume over time

The gel recipe made included xanthan gum and consolidated mud from port of Rotterdam, 3%wt of dry XG and 10%wt dry solids in the final gel sample. In total 1.2 kg of the gel was made, placed in a mold, and cut into 4 four semi-cylindrical specimens, each weighing between 150-300g. The remaining quantity was kept for rheology characterization to confirm homogeneity and density testing (1.11 g/ml for XG3Mud10).

The volume of the barrier was calculated by measuring the height, length and width of the barrier through pictures taken with a stable camera at 1h intervals. Figure 6.5 shows an estimation of the volume change of the four specimens over time. The results are presented in a relative form to correct based on the initial volume. The volume was estimated by multiplying the area of the barrier cross section with total length, L. The cross-section area was calculated as a semi ellipse, with maximum width, D and maximum height, H. The following formula was used:

$$V = \frac{\pi}{2} \cdot \frac{D}{2} \cdot H \cdot L$$

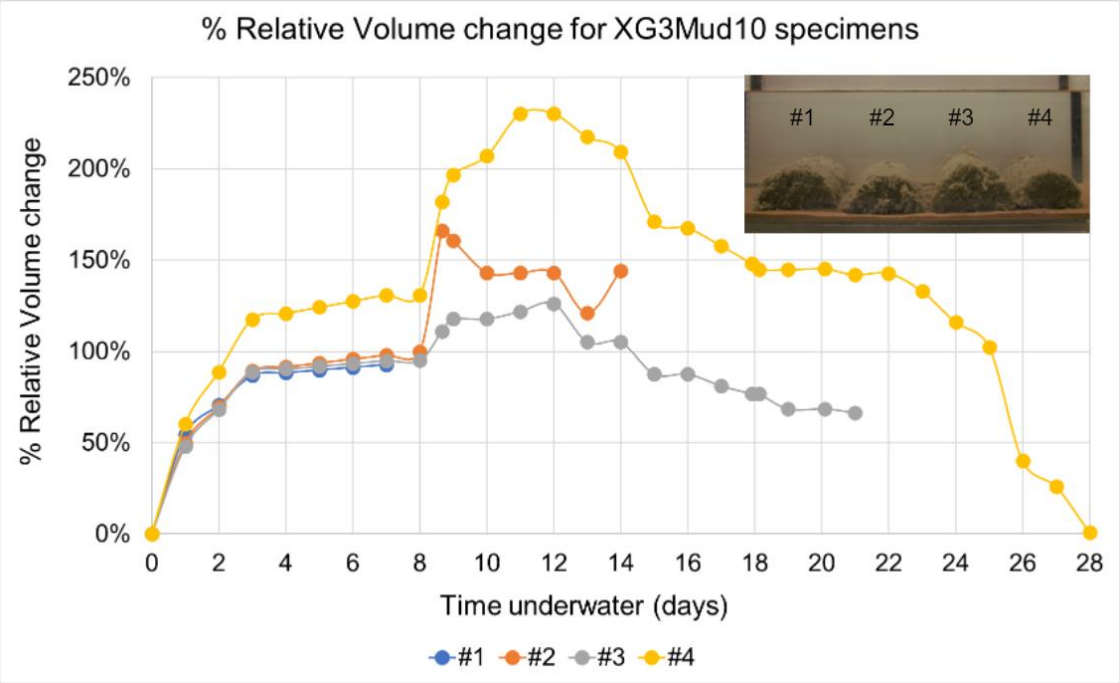


Figure 6.5: Relative volume change of gel barrier specimens over time

Out of the four studied specimens, #1 and #2 (as shown in the picture above) are similar in size with an initial volume of 210ml. However, #3 is slightly bigger with 260ml and #4 slightly smaller with 160ml. This is related to the way the cylindrical sample was cut. By analyzing the Figure 6.5 above, the smaller sample (#4) swells more than 200% of its original volume, whereas the rest #1, #2, #3 exhibit similar increase around 120% within the first week. This indicates that the swelling of the gels is scale dependent, as higher surface area results in great water uptake.

Every week one of the specimens was removed from the tank to be studied rheologically and assess its strength, density and erosion threshold. The water in the tank has been changed every week as the water becomes too dirty to observe the specimens. Irregular swelling caused on day 8 after the water change in the tank. This fast volume expansion lasted approximately 5 hours and took place overnight (6 hours after the water change). It is speculated that the observed effect is associated with osmosis, as salt concentration in the sample might be even higher than 2.5%. Once swelling occurs (week 2) the gel starts to reduce in volume and the shape is altered. With this non-optimized recipe (XG3Mud10) the lifetime of the barrier is estimated to be around 4 weeks. Therefore, it is recommended to create a diffusion model to estimate how the gel barrier volume will change under osmotic effects.

6.5.2. Strength of the specimens over time

Once the specimen was removed from the water tank, it was characterized rheogically to estimate its stiffness. The barrier was carefully sectioned in various pieces and cylindrical coordinates have been given to each area to identify the samples. In this way, it is possible to estimate the profile of the strength as a function of distance from the core (radial distance, R) and the length of the specimen (L). Slices of the barrier were taken along the L axis from the center, and front edge of the specimen. Additionally, each slide was sectioned across the radial axis R, and a sample was tested from the left, middle and right side. The tests took place for 4 weeks in total and the results for the center slice of the specimens are presented in Figure 6.6.

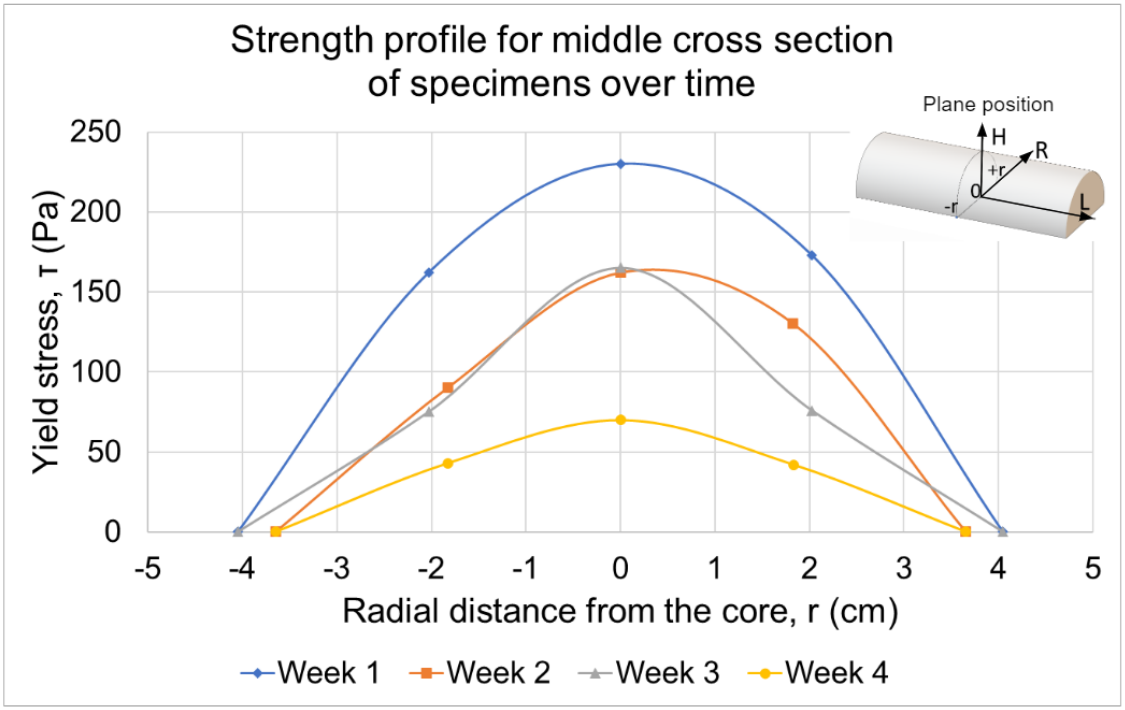


Figure 6.6: Weekly change in yield stress profile over radial distance

A visual depiction of the rheological strength profile for the whole semi-cylindrical specimens is shown in Figure 6.7. This depiction has been made graphically without the use of specific software; thus the pictures are meant to provide only an estimation. To complete the profile Plane symmetry has been used (across the R/H plane) to estimate the profile in the back side of the specimen.

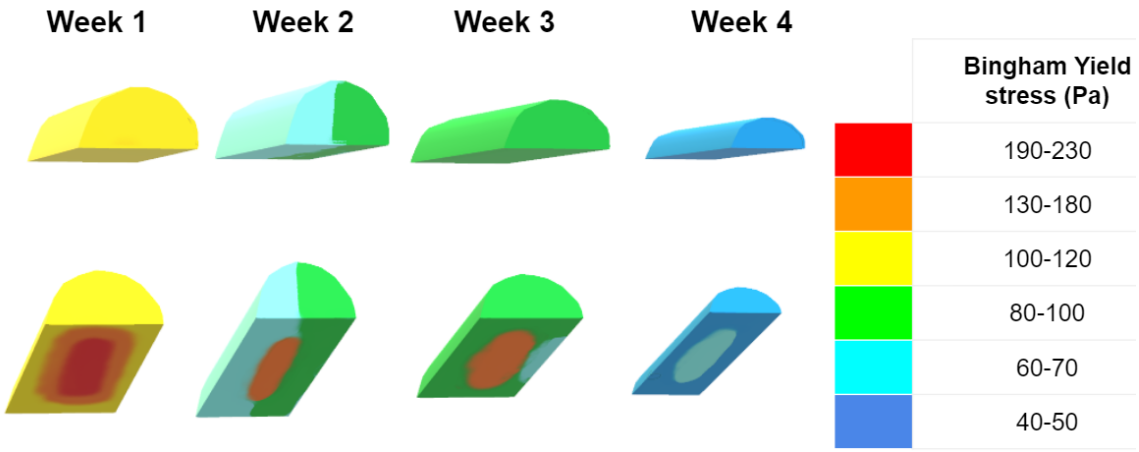


Figure 6.7: Visual of weekly strength profile at various areas

With respect to the strength profile in the center of the gel, the maximum yield stress has been decreasing overtime. Considering that the initial gel strength on the manufacturing day was 250Pa, the yield stress deteriorates initially at a slower rate (-10%/week) for week 1 and 3 and faster in week 4 (-50% in comparison to week 3). The data in week 2 suggest that the barrier is significantly more degraded than expected and this can be attributed to the irregular swelling observed in the tank on day 8. This sudden change in volume, moved the barrier significantly, making it fold over its center, falling on the right side. This disruption exposed the core of the sample in water and as a result more XG dissolved. More mud particles were no longer bonded strongly with the XG system and escaped from the gel. This is a possible explanation for the observed lower yield stress in week 2.

6.5.3. Erosion tests

In addition to the rheological measurements, erosion tests took place for specific samples to determine the shear rate under which the barrier will start eroding and dispersing. The set up used (Figure 6.8) included a previously calibrated pump, that can inject a water stream at various speeds through a pipe (6.4mm inner diameter). A small piece (around 5g) was taken from each specimen, once from the core of the sample and once from the edge. The samples were placed 2cm in front of a known speed water stream. Figure 6.9 shows an example of erosion test with a yield stress of 160Pa. The following equations was used to convert the pumping speed to shear rate and the water speed of the water 2cm from the inlet point.

$$\dot{\gamma} = \frac{4\,Q}{\pi\,r^3} \;\; and \;\; u = \frac{Q}{\pi\,r^2}$$

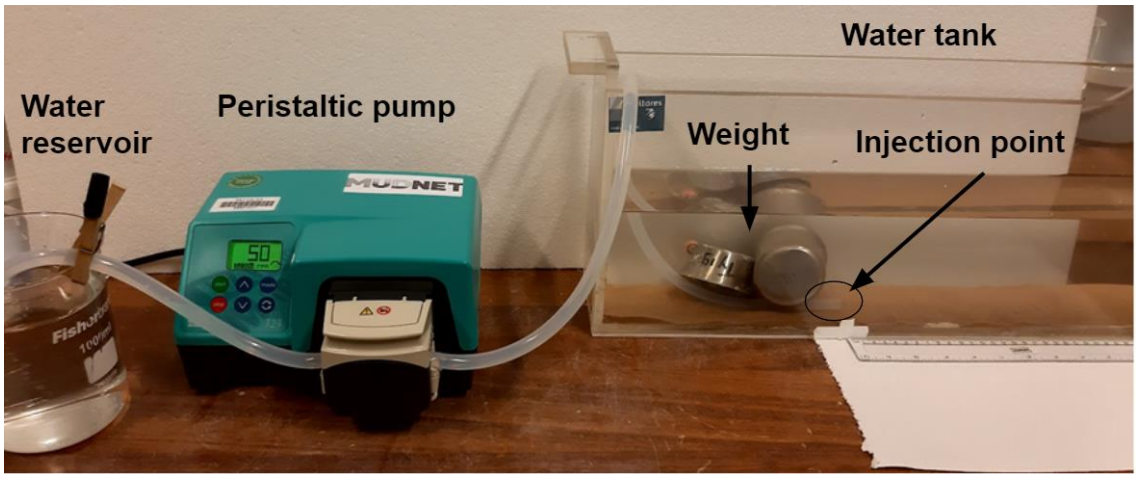


Figure 6.8: Experimental setup for erosion trials

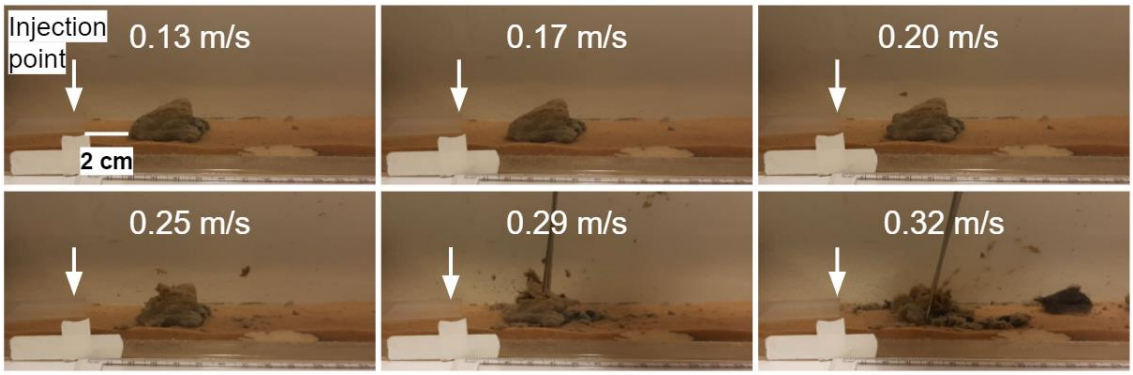


Figure 6.9: Visual observation of erosion on 160Pa gel. The white arrows show the injection point of the water stream.

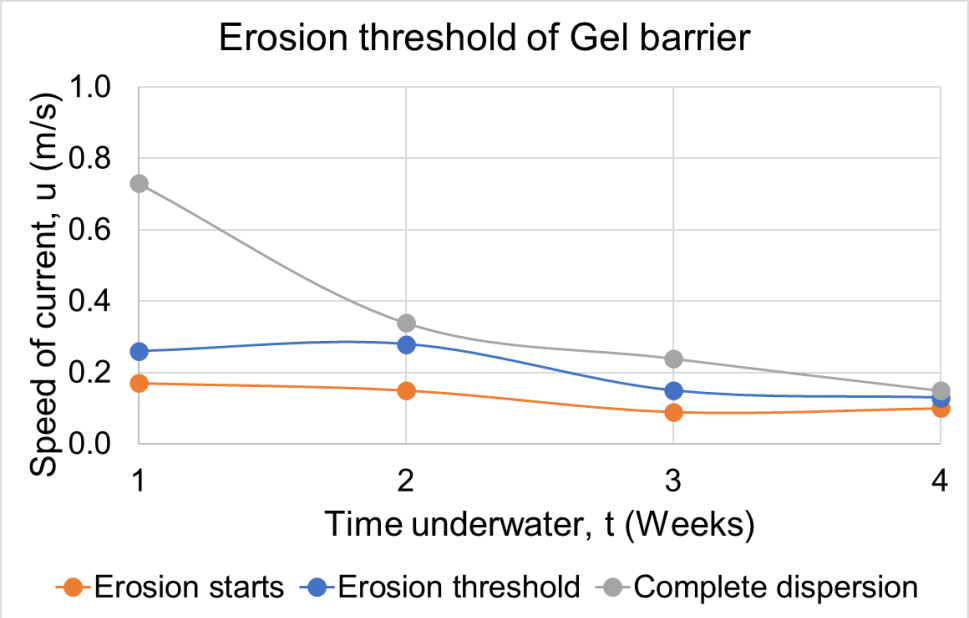


Figure 6.10: Weekly changes in erosion for different speeds of current underwater

Figure 6.10 shows that when the 1st week core sample is exposed in 0.2 m/s speed current, erosion will start occurring at its surface, with tiny gel blobs starting to detach from the gel structure (a few mm size). The erosion will become easily noticeable at 0.3m/s (bigger chunks detach, 5-10mm scale), whereas with higher speed currents the barrier will totally disperse at 0.7 m/s. The erosion threshold slowly drops the longer the gel remains underwater. On Week 4 the barrier will disperse at speeds above 0.1 m/s.

6.5.4. Density profile

Finally, density measurements were made for each of the gel samples, when freshly prepared and after 1-4 weeks underwater. Different areas of the specimens were collected and mixed to perform the density tests. A syringe was used to estimate the weight and volume of various samples and 5-15 density measurements were performed to account for statistical error. The average value of density is shown right next to the experimental sets.

The initial density of the gel (XG3Mud10) is 1.12 g/ml and decreases slowly each week. An exception can be seen for week 2, as the irregular swelling led to mud escaping from the gel as described earlier. In the last week of the trials, the sample that was isolated was previously filtered to remove any sand particles mixed with the gel.

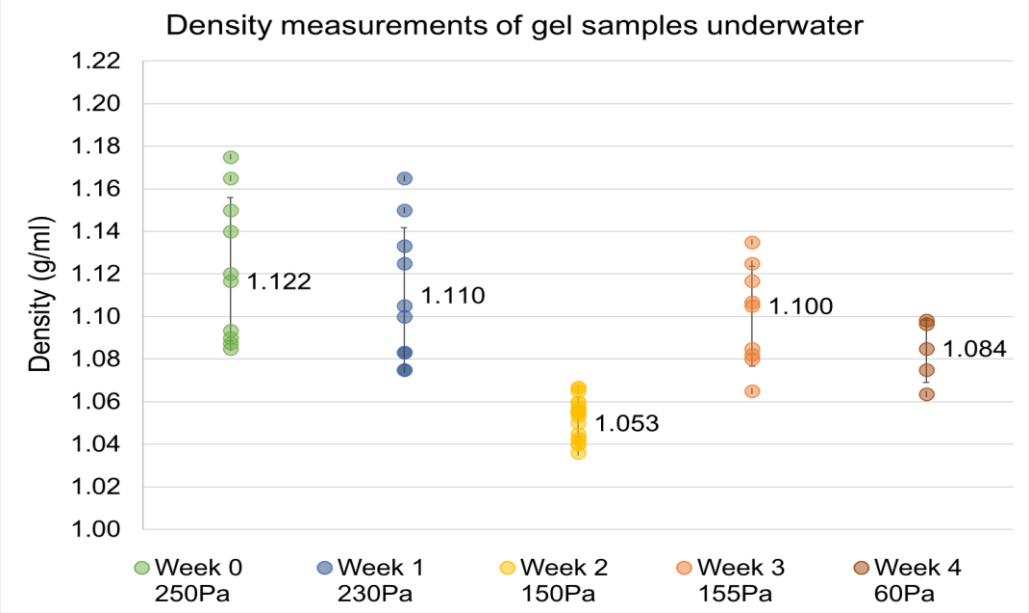


Figure 6.11: Density of gel specimens over time in 2.5%w/w NaCl water

Based on the above observations a mechanism was identified that can possibly explain this behavior. It is assumed that when the gels are placed underwater, swelling occurs as water molecules are absorbed from the polymeric network of Xanthan gum. The difference in salinity between the sample and the core can also cause this effect. Once full hydration has occurred, the network of XG is loosened and can easier escape the system by dissolving in the surround water. This will leave behind loose particles of mud and as a result the density in is dramatically reduced at the outer surface of the gel. In the core, however of the specimen the mud particles are retained, therefore the density there remains relatively stable. This mechanism could also explain the deteriorated gel strength and density that was caused by the disruption in week 2.

Chapter 7: Economical feasibility

In this paragraph a comparison of the material cost of the gel product will be presented for the identified gelation ingredients. The main cost driver was identified to be the gelation agent used in the formulation and therefore the estimation aims to compare final gel products that do not contain any solids.

7.1. Material cost

In this estimation, in all examined cases the concentration of the gelation agent was chosen so that the end-product is a gel with a yield stress of 80-100 Pa. The concentration of the gelation agent was determined either experimentally or from literature review, as shown in the Appendix (Table A4). The comparison can be found in Figure 7.1 below.

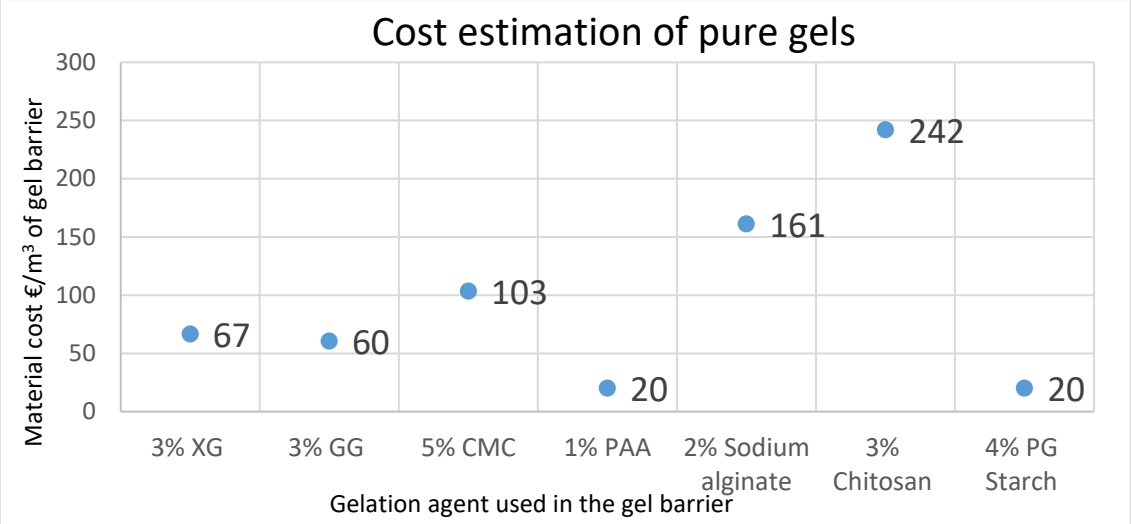


Figure 7.1: Comparison of commercially available gels that result in an >80Pa gel barrier.

From the Figure 7.1, it can be concluded that sodium alginate and chitosan are very expensive choices for a gel barrier because of the high unit cost of these ingredients. Others like pre-gelatinized starch are cheaper, however additional energy is required for the pretreatment of starch to make it soluble in cold water. Polyacrylic acid (PAA) is also a low-cost solution with a cost of only 20€/$m^3_{\text{of barrier}}$. Even though it is non-toxic and slowly biodegradable, PAA is not recommended to be used in the gel product at the moment because of environmental concerns (Appendix A1). The use of PAA could become possible if faster biodegradability is achieved with monomer modifications.

The use of XG, GG or mixtures of the two is a feasible solution. Additionally, CMC could potentially also be used especially because of its better microbial stability. The concentration in this case should be studied further and possibly mixed with higher content of mud to achieve the desired material strength.

With respect to Kaumera, the current selling price is in the order of a few euro per kilo of final suspension. However, the produced Kaumera today has a low solids content (around 8%w/w)

without further processing. Considering the big volumes of the gel that are required (thousands of m^3) for a barrier, the use of Kaumera at this scale seems not yet economically feasible. However, research to increase the percentage of dry solids and development methods to dry Kaumera are ongoing, which could offer more opportunities for Kaumera in the future. Some considerations about the technical feasibility of Kaumera are discussed in Chapter 9.

As explained earlier in this report, the stiffness can be tuned by the addition of mud in the formulation. According to the end-of-waste framework that is presented in Chapter 3, dredged mud can be considered a type of waste that is being reused instead of disposed. For this reason, the cost of mud in the formulation was excluded from the calculation.

7.2. Effectiveness of gel barrier in mud reduction

A sensitivity analysis was performed to assess under which conditions the use of the gel barrier will result in profit for port of Rotterdam. The factors that were studied were the lifetime of the barrier and the efficiency of the product in reducing the amount of dredging required. The results are provided in an annual basis, based on the model for savings that is described in paragraph 3.5. This includes the annual **material**, **manufacturing**, **application** and **cleaning** cost for the gel barrier(s).

The analysis was conducted for 1, 5 or 10 gel barriers per year assuming that each time, the same volume of 5,500 m^3 barrier is applied on the same location in Botlek area. The results are provided in Figure 7.2.

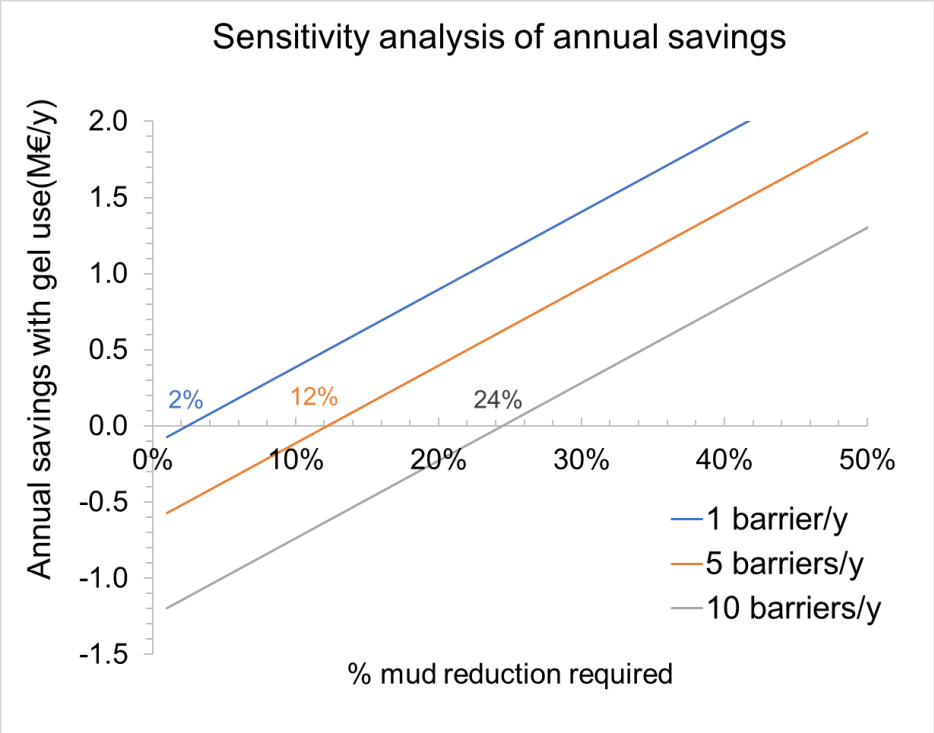


Figure 7.2: Sensitivity analysis of annual savings as a function of gel application frequency and mud reduction efficiency

Figure 7.2 shows the amount of money that can be spared from reduction in dredging operations in the port of Botlek. The graph helps define the degree (%) of mud reduction that

the barrier needs to achieve to be economically profitable. The highlighted values next to each line show the percentage of mud reduction that is required to balance the total savings from dredging with the total cost of material, manufacturing and application. Therefore, to reach the breakeven point with 5 barriers a year, the efficiency of the barrier needs to be 12%, or the barrier will result in loss for the port. The break even for 1 and 10 barriers per year is 2% and 24% respectively.

To achieve the target of 5% annual cost reduction from dredging operations, a total of 1.8M€/y need to be spared per year. This can be achieved for example with the use of 5 barriers/y with an efficiency of 48% reduction of mud, or with the use of a single barrier per year with an efficiency of 36% mud reduction.

To visualize how the barrier will result in reducing the amount of incoming mud in the port, a small-scale experiment was performed in the Deltares lab. A gel barrier (150ml) was placed across the cross section of a 5L-water tank as it is shown in Figure 7.3 below. A pump was used to inject diluted mud suspension, at 20rpm. This corresponds to shear rate = 280 s^{-1} at the exit of the tube, based on the pipe characteristics.

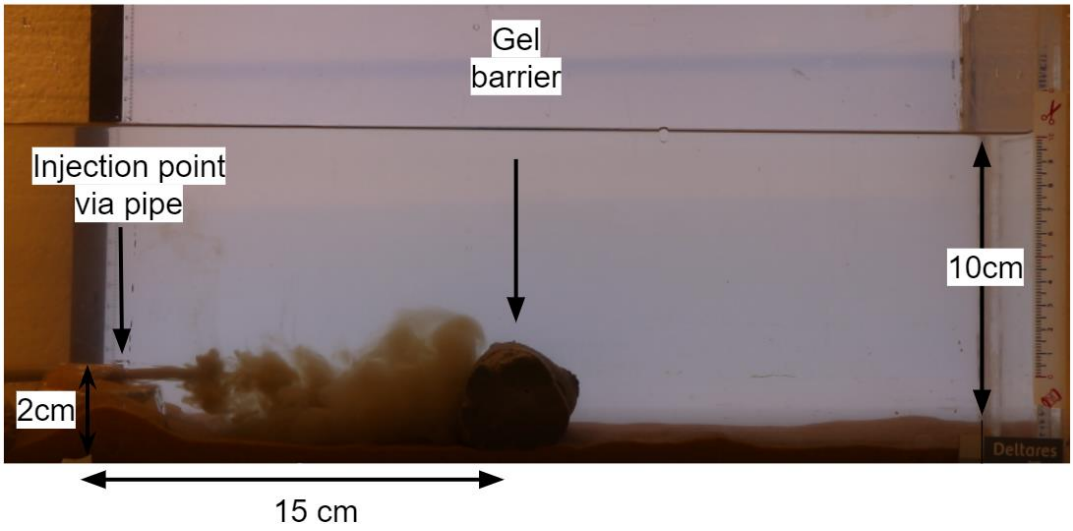


Figure 7.3: Mud injection towards a gel barrier sample

This trial serves as a preliminary investigation of how the barrier interacts with mud particles and if it is possible to hinder the spread of mud with a barrier. For 20 rpm pumping speed the mud current partially overshoots the barrier, however when lower speed was used (10rpm) the mud is contained on the left side of the barrier. This experiment also showed that mud does not stick to the barrier. Therefore, it seems that the gel barrier cannot hinter all incoming mud but can potentially prevent a percentage of sediment from spreading further in the port. This barrier could also be applied to prevent the spread of a density current. The actual efficiency of the barrier was not quantified, and the data generated can be used to illustrate how the concept is going to work.

Chapter 8: Environmental considerations

In this chapter an overview of the environmental impact of the gel barrier will be presented by assessing part of the CO2 emissions that will be generated in the process making of the barrier. A comparison will be made for Botlek area between the emission for application and the emissions that will be spared because of the reduction in dredging. Additionally, considerations on how to repurpose the barrier at the end of its life will be provided for circular economy.

8.1. CO_2 emissions related to the gel barrier use

As it has been discussed in paragraph 7.2, the use of the gel barrier in the Rotterdam port area is expected to reduce the incoming sediment into the smaller channels. This reduction will spare energy and generation of CO2 emissions. For the scenario where 10 barriers/y are built in Botlek, the barrier efficiency needs to be 45% to spare 1M€/y. A comparison of the CO2 emissions generated within the Rotterdam port area has been made for the three different application strategies that have been discussed in section 5.2. The results are shown in Figure 8.1, and the list of assumptions made for this estimation of CO2 emissions is the following:

- Assuming a barrier efficiency of 45%, the gel product will result in 45% less sediment accumulation in the Botlek area. The annual dredging volume of sediment in this area has been previously estimated to be 2Mm^3/y. Therefore, approximately 0.9Mm^3/y of sediment will be prevented with the use of the barrier.
- The emissions produced with current dredging operations result in an average of 3 $KgCO_2/m^3$ of dredged sediment on a desired location (van der Bilt, 2019).
- The heavy machinery used in the port area operate with gas/diesel oil. The emission factor for estimating land and waterway transportation was 2.61 $KgCO_2$/l of fuel spent (Zijlema, 2021).
- The mixing energy from offsite production was estimated to originate from natural gas and the emission factor was 0.23$KgCO_2$/kWh (Zijlema, 2021).
- The footprint for each application strategy considers that the gel barrier is manufactured, placed, and removed 10 times a year from the desired port location.

The comparison made in Figure 8.1 includes two scenarios, a high scenario (green bar), where the presence of the barrier reduces the accumulated sediment by 45% and a low scenario (blue bar) with 5% reduction. The graph shows that in Botlek alone, for the high scenario the annual CO_2 emissions can be reduced by 2,700-300 = 2,400 CO_2 t/y by placing a barrier in the inlet of the channels. Additionally, looking at the low scenario, the efficiency of the barrier in mud reduction should be at least 5%, for the gel barrier concept to be CO_2 neutral.

The application strategy that has been previously discussed includes the pretreatment, manufacturing, transportation and placement cost for the final gel product. It also considers the cost of removing any remaining barrier fragments at the end of their lifetime. The emissions related to the manufacturing of xanthan gum has been excluded from the above estimation as this will vary according to the supplier.

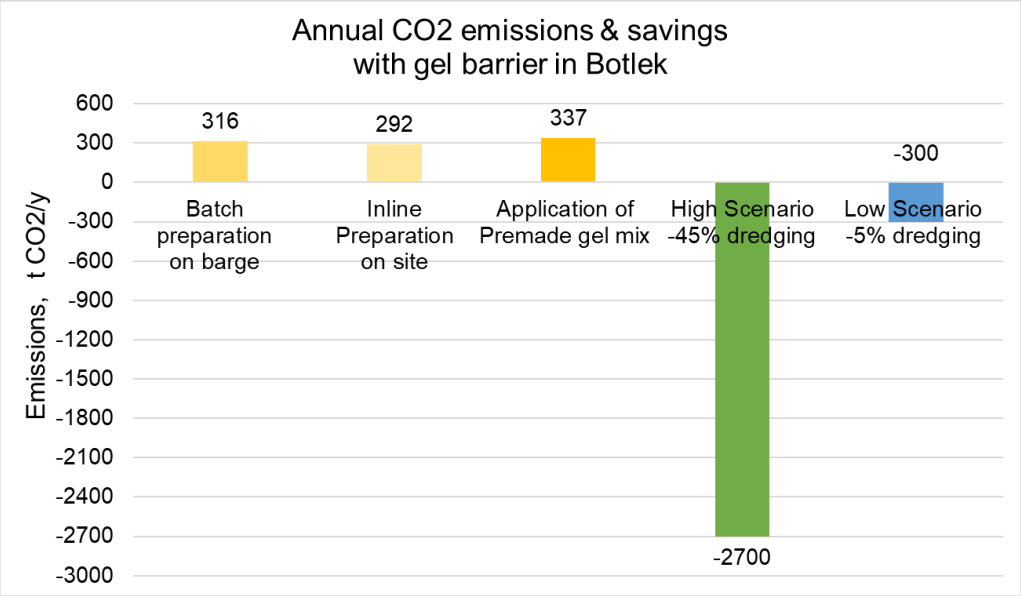


Figure 8.1: Comparison of CO2 emissions and savings for the different application strategies

8.2. Repurposing the gel barrier

The main ingredients proposed for the gel barrier recipe are xanthan gum and dredged mud from the Rotterdam port area. Towards the end of its lifetime, the barrier is expected to decrease in volume, as xanthan gum is slowly dissolving, and finally leaving behind loose particles of mud. At the end of the product's life the remaining gel fragments are to be collected into a sedimentation trap and after dredging get disposed to the open sea. This approach will yield CO_2 emissions as previously presented in Figure 8.1. However, more options with respect to circular economy are proposed below:

- The **first approach** that is suggested is to **rebuild the new gel barrier on the same position** without removing any excess of the previous barrier. This procedure will ensure that a physical barrier remains in place for longer time and will eliminate the need of removal of the barrier with dredging. It is expected that cleaning will be required once a year and the CO_2 emissions will be further reduced by 30%, and the annual footprint of the barrier will be 200-240 tCO_2/y.
- The **second suggestion** is the **removal of the gel barrier pieces** with dredging which can later be **applied on supporting dykes** at other locations in the Rotterdam port area. It is recommended to investigate the potential improvement in soil stability that can be achieved with the presence of polymer on the new locations.
- The **third strategy** includes the use of the **remaining fragments** as a **binding agent to heavy metals**. According to literature xanthan gum can potentially bind to divalent cations of metals some of which include heavy metals such as Cd^{2+}, Cu^{2+}, Zn^{2+} Pb^{2+} (Bergmann et al., 2008). Therefore, the residue from the gel barrier that still contain xanthan gum can be added to existing contaminated sediment reservoirs to assist in the removal of heavy metals. To achieve the desired binding and removal capacity a new study should take place to assess the technical feasibility of this application.

Chapter 9: Kaumera investigation

Kaumera is a versatile product that contains a mixture of proteins, polysaccharides, and inorganic compounds as described in paragraph 3.4. Although it is already used in small scale commercial applications, the current annual production rates in combination of the low concentration of solids in the final Kaumera suspension makes the unit cost too high to be used as a gelation agent in the barrier for the Rotterdam port area. Therefore, the purpose of this chapter is to investigate the rheological characteristics for the Kaumera at different conditions and provide development direction for future production. The effect on the rheology of the following parameters has been examined:

- Temperature effect for **thermal drying** of **Kaumera** suspensions at 60 and 105°C.
- Dry Kaumera powder and **flocculation** of clay
- Effect of **increasing Kaumera concentration** in mixtures with **Kaumera** and **Clay**.
- Effect of **Ca^{2+} concentration** on the surface **charge** of diluted **Kaumera** samples.
- Comparison of yield stress for **mixtures with clay** and **basic or acidic Kaumera**
- Strength of **XG:Kaumera** system (1:1 ratio) for different **pH** and **surface charge**. (Xanthan gum combined with positively- or negatively- charged Kaumera).

9.1. Drying temperature effect on rheological properties

In this study, two Kaumera samples with a fixed concentration of 7%w/w have been prepared by dispersing dried Kaumera at 60 and 105°C in deionized water. The mixtures were stirred at 20°C for 24h before density, pH and rheological properties were tested. The dry powder of Kaumera was obtained by placing Kaumera suspension from Zutphen in the oven for more than 24hours. The obtained dried solid was grinded and sieved through 1mm and 425 μm sieves respectively. Loss on drying tests show that 5.47% of moisture is still present in the 60°C dried Kaumera powder. Thus, the weight of the powder added to the final suspensions has been adjusted to account for present of water in the powder. The final powder and suspensions after stirring can be seen in Figure 9.1.

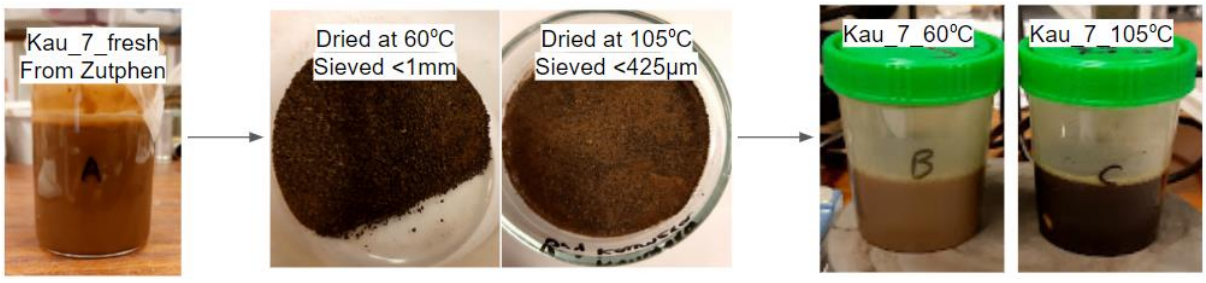


Figure 9.1: From left to right; Acidic Kaumera suspension from Zutphen, dried and sieved Kaumera powder obtained with thermal drying, suspensions made by dispersing dried Kaumera in water

The controlled shear rate graphs that were obtained when testing the above samples (Figure 9.2) indicate that the yield stress and viscosity of the suspensions is reduced roughly 10 times

with the Kaumera powder obtained at 60°C, whereas the suspension with Kaumera at 105°C shows absence of viscoelastic behavior and rheological properties close to water, with a viscosity of 0.7 mPas at 20 °C. Table 9.1 provides a summary of the characteristics for the three suspensions. Additionally, some measurements in particle size have been made by W. Ali, PhD researcher at CITG-HE department of TU Delft and member of FLOCMud team. Two different batches of Kaumera were tested to assess the effect that Kaumera has in clay suspensions (Figure 9.3):

- Batch v1 (from the municipal wastewater treatment plant in Epe) and
- Batch v2 (from the industrial wastewater treatment plant in Zutphen)

Table 9.1: Summary of characteristics for the suspensions made with dried Kaumera.

Sample Code	Sample description	Concentration %w/w	pH	Density g/ml	Bingham Yield stress (Pa)
Kau_7_fresh	Suspension from Zutphen	7.22	2-3	1.076	3.670
Kau_7_60°C	Dried powder at 60°C in DIW	7.00	2-3	1.055	0.096
Kau_7_105°C	Dried powder at 105°C in DIW	6.90	2-3	1.045	0.002

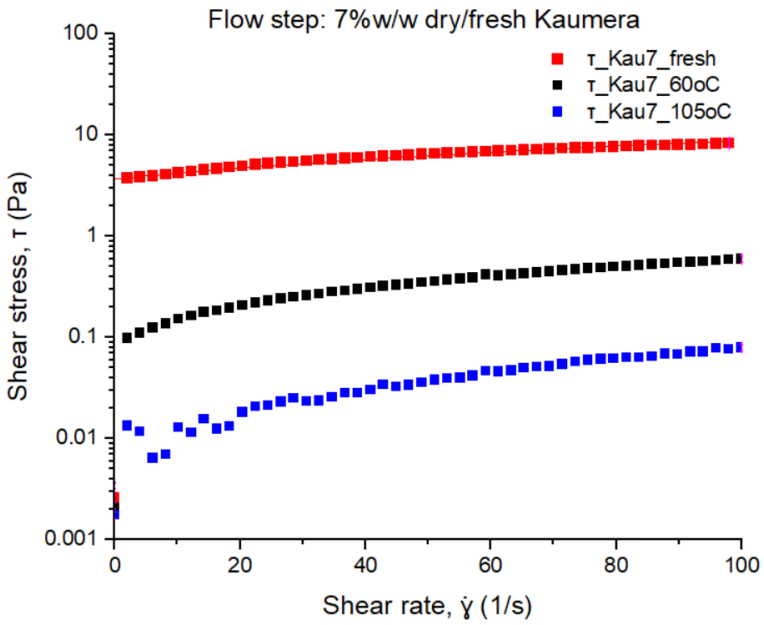


Figure 9.2: Comparison of rheological strength for 7%w/w suspensions with fresh and dry Kaumera

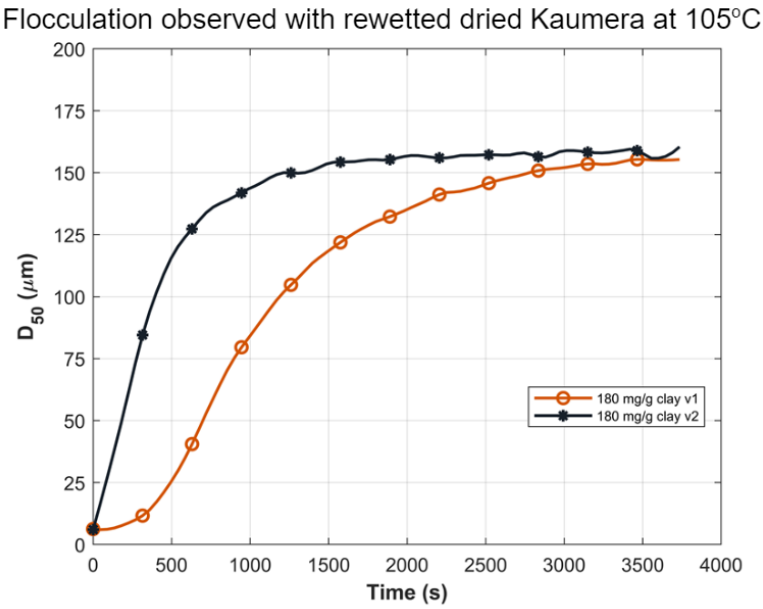


Figure 9.3: Rewetted dried Kaumera results in flocculation of clay particles for EPE (v1) & Zutphen (v2) batch

It can be concluded that thermal drying is not appropriate method for the storage of Kaumera in powder form. The network structure is irreversibly altered and therefore the yielding properties of the rewetted Kaumera are deteriorated.

It is suggested that the crosslinking degree between amino acids and polysaccharides is significantly altered resulting in a less strong viscoelastic network. A Maillard reaction between the previously mentioned groups is speculated to occur during the heating process.

However, the particle size measurements in clay suspensions suggest that dried Kaumera can be used as a flocculent, as it increases the particle size to 150µm. Graph 9.3 shows that the same final floc size can be achieved with two different batches of Kaumera. The Kaumera batch from Zutphen seems to yield faster flocculation.

Looking to Kaumera as a mixture of chains containing different building blocks, it is speculated that after the drying process some of the building blocks are destroyed leading to breaking of the long chain molecules. Even though this effect will lower the strength of the network, it can allow the active blocks for flocculation to interact with clay particles and therefore create flocs.

9.2. Effect of Kaumera concentration on the strength of Kaumera: Clay gels

The second investigation that was conducted aimed to show how the increasing content of Kaumera in 22%w/w Clay suspensions can affect the rheological properties of the system. The current suspension of Kaumera that is manufactured in Zutphen is not concentrated enough to yield stiff gels that could be used as a gel barrier. For this application the stiffness of the product mixture should be in the order of 300Pa, whereas the current values of the suspension with 7% Kaumera suspension and 22% Clay reach a value of 30Pa. Thus, in the present study the dried 60^{o}C Kaumera powder was used as the main Kaumera source in the tested samples.

As described in the previous paragraph it is expected that the examined system will be less strong than an equivalent system made with fresh Kaumera suspension. Hence, the results are meant to be used only as a comparison between the presented samples and cannot be extrapolated to samples made with Kaumera suspensions with solids concentrations more than 7%w/w.

Three samples were manufactured by mixing Clay suspensions with dry Kaumera powder at 5, 10 and 20%w/w concentration. The samples were fully characterized using a Haake-Mars rheometer with bob and cup geometry. The yield stress measurements were estimated by fitting the bingham model on the data (Table 9.2). A summary of the yield stress of Kaumera as a function of concentration is shown in Figure 9.4.

Table 9.2: Rheological characteristics of samples with clay and Kaumera

Measurement	Strength	Kau5Clay22	Kau10Clay22	Kau20Clay22	Clay22
Controlled shear rate	Yield stress (Pa)	20	60	960	0.5

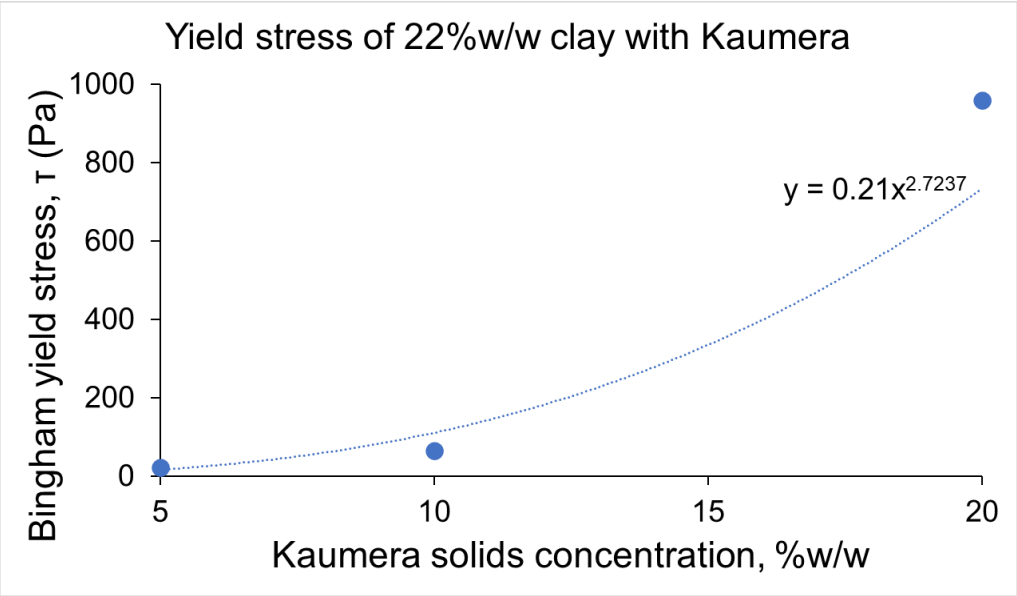


Figure 9.4: Strength of 22%w/w clay suspensions with increasing Kaumera concentration

The experimental data suggest that the addition of Kaumera at 22%w/w Clay suspensions significantly increases the yield stress of the samples at concentrations higher than 10%w/w

Clay. This observation indicates that a mass ratio of clay/Kaumera close to 1:1 strengthens the network by 2000 times in comparison to the initial 22%w/w Clay suspension, whereas 2:1 ratio result in 120 times higher dynamic yield stress values. These preliminary results suggest that there is an optimum ratio between clay particles and Kaumera. Should clay and Kaumera systems be of interest for structural applications, it is therefore recommended to investigate this interaction further at even higher mass ratios.

Combining these results with the previous paragraph, it is expected that if samples could be made with 20%w/w Kaumera suspension they would exhibit much higher yield stress, possibly 10 times higher. At the current development stage of Kaumera, concentrating the product further with the centrifugal filtrations can result in slightly higher concentrations than the 7-8%w/w suspension. However, a key development direction for the Kaumera project would be to increase the yield in the final suspensions to 20%w/w.

Even though the results obtained with dried Kaumera are not representative of the behavior of concentrated liquid Kaumera suspensions, the rheological data can provide an indication of the effect on concentration at higher mass fractions.

9.3. Effect of Ca^{2+} in zeta potential of diluted Kaumera suspensions

Kaumera as a mixture of proteins and polysaccharides exhibits unique characteristics. Ionic interactions between the long chain molecules can potentially result in partially cross-linking of the chains and stronger viscoelastic network. Thus, studying the surface charge of Kaumera can provide us with an indication of how ions affect the charge and possible the agglomeration of Kaumera particles or cross-linking of Kaumera regions. In this paragraph firstly the surface charge of Kaumera has been studied by dispersing the suspension from Zutphen in DIW and measuring the zeta potential of the sample. Secondly, the changes in zeta potential have been monitored for the first 20 minutes of adding Calcium cations at increasing concentrations.

The measurements have been performed with the ZetaCompact instrument, which can apply electrical field on a cell containing the sample and with optical observation studies the velocity profile of the particles moving under this electric field. To be able to better observe individual particles in the suspension, the prepared samples had a low concentration of Kaumera (0.04%w/w of Kaumera solids). The initial pH of all samples was recorded, and conductivity was monitored along the measurements. The pH values for all samples ranged from 3.9-4.1, whereas conductivity varies according to the concentration of Ca^{2+} added to the sample. A concentrated solution of calcium chloride salt (40mM) has been previously prepared by dissolving solid $CaCl_2.6H_20$ salt in DIW. The required amount of the 40mM solution has been added to a sample to create 0.04%w/w Kaumera samples with 1mM, 5mM and 10mM Ca^{2+}.

The purpose of the experiment was to study the time dependency of calcium cations concentration at 0.04%w/w Kaumera suspensions. Thus, the moment of adding the concentrated $CaCl_2$ solution into the Kaumera sample is t=0. Then measurements of zeta potential have been recorded every 2 minutes for a total of 20-25 minutes per sample. The results of the conductivity and zeta potential are available in Figure 9.5 and 9.6. The table 9.3

shows the conductivity values that are recorded in comparison to the theoretical value of the $CaCl_2$ solution.

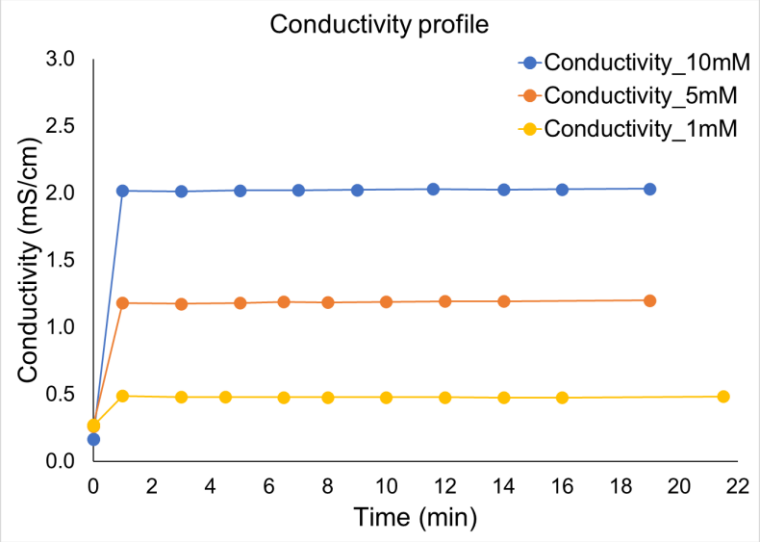


Figure 9.5: Conductivity profile during the zeta potential measurements

Table 9.3: Comaprion of theoretical and experimental conductivity of the kaumera/Ca^{2+} samples

Theoretical conductivity $CaCl_2$ in MiliQ (mS/cm)	**Experimental conductivity 0.04%w/w Kaumera in MiliQ**	**Theoretical Total conductivity of mixture (mS/cm)**	**Experimental Total conductivity of mixture (mS/cm)**
10mM: 0.995	0.260	1.255	1.188
5mM: 0.417	0.260	0.677	0.628
1mM: 0.235	0.260	0.495	0.479

From the graph in Figure 9.5 it can be seen that the initial conductivity changes as the calcium solution is added into the kaumera sample at t=0. For the remaining measurement time 2-20min the conductivity remains stable for each individual sample, whereas the higher the concentration of calcium cations in the final solution, the higher the value of the final recorded conductivity. Additionally, the experimentally recorded conductivity values are similar to the ones predicted theoretically for $CaCl_2$ solutions once the conductivity of the diluted Kaumera supension is added.

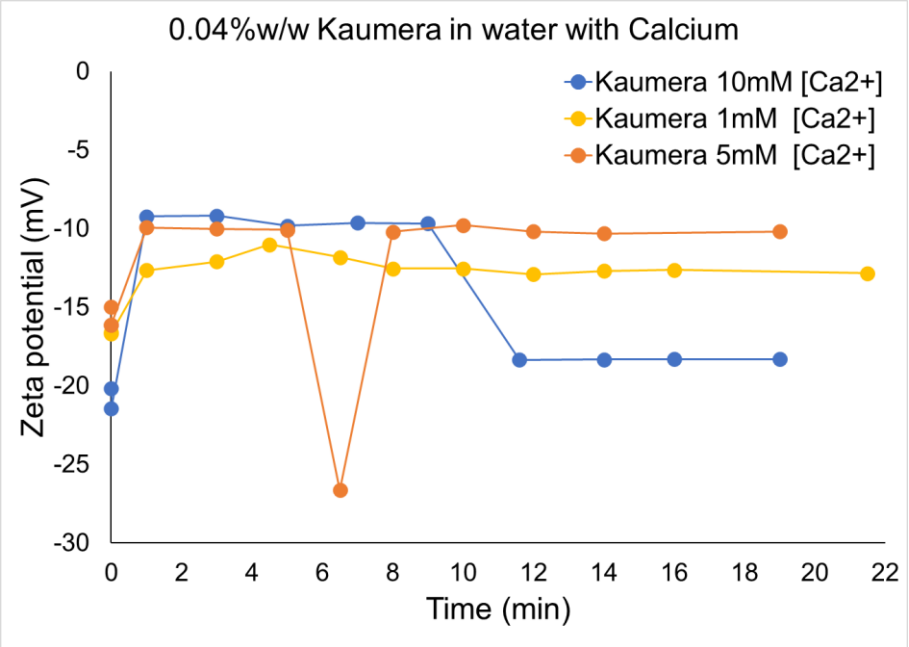


Figure 9.6: Time dependency of Zeta potential profile for Kaumera samples with added Ca^{2+}

By observing the graph in Figure 9.6 it seems that adding Ca^{2+} in diluted kaumera results in a change in the zeta potential for 10mM after 10 minutes of addition. This change corresponds to a mass ratio of kaumera: $CaCl_2$ = 1:40, whereas in the case of kaumera with 1mM [Ca^{2+}] (mass ratio 1:4) this change is not observed. For the intermediate mass ratio of 1:10 kaumera:$CaCl_2$ (5mM) a sudden change is observed at 7 minutes. As a possible explanation for this effect, flocculation might be starting to take place between the kaumera particles. This would result in less suspended particles on the mixture, possibly creating a supernatant with unflocculated particles of higher surface charge.

A less probable explanation could refer to a reaction taking place between the calcium cations and protons in the Kaumera network. However, since acidic Kaumera has been used, the Kaumera particles are not fully dissolved in the water and the reaction might not be occurring.

9.4. Samples with Clay and Basic Kaumera

As it has been previously reported by M. Wyszyńska, a previous PDEng trainee, the use of Kaumera under basic conditions has a beneficial impact on flocculation of clay suspensions in comparison to the acidic Kaumera form (Wyszyńska, 2020). Based on this indication, samples with 22% Clay and 5% Kaumera have been made, once with Kaumera in acidic form and once with basic Kaumera. The basic Kaumera sample has been prepared in the lab by following the alkalization step of the manufacturing process. The final sample contains around 7%w/w of dry solids. The basic suspension has been used on the same day for manufacturing gel samples containing 22%w/w clay and 5%w/w basic Kaumera. The rheological profile of the sample has been compared with a gel having the same ratio and concentrations of acidic Kaumera solution. The results are depicted in Figure 9.7. As a reference the yield stress obtained with a suspension of 22%w/w Clay is around 0.5Pa.

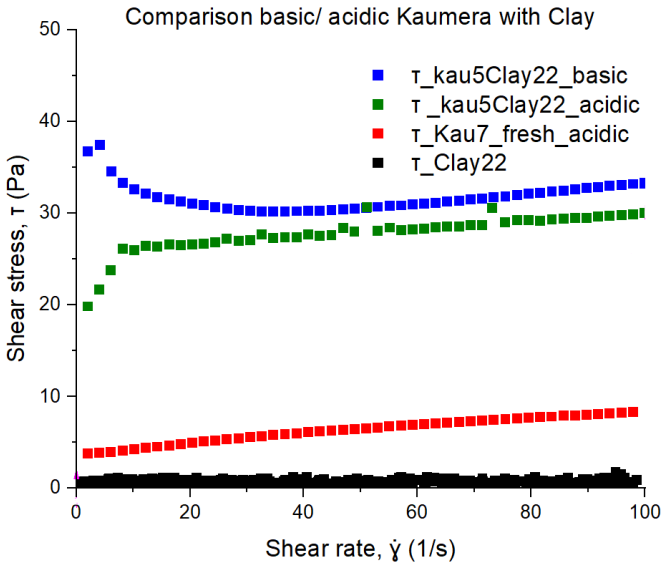


Figure 9.7: Shear stress comparison for gels made with clay and basic or fresh acidic Kaumera

The graph above indicates that gels that were made with basic Kaumera exhibit slightly stronger rheological properties than gels with acidic Kaumera. By alkalization of the initial Kaumera suspension, a form of dissolved Kaumera is formed that can interact more strongly with Clay particles and other polymeric chains. For the experimental data it is concluded that a 30% increase of the rheological properties is expected when clay is combined with basic Kaumera over the acidic form.

These results have been obtained by using parallel plate geometry and allowing sufficient equilibration time between loading and the start of the measurement (10 minutes). Similarly, to what have been presented on the previous paragraphs finding the optimum ratio between clay and basic Kaumera is required to ensure better rheological properties. The above preliminary test provides a good indication that the use of basic Kaumera should be preferred over the acidic fresh form.

9.5. Strength of XG: Kaumera systems

This paragraph is focused on studying the behavior of a system containing pure XG polymer and Kaumera in mass ratio 1:1. Kaumera seems to be a good dispersion agent for gums as the water that is incorporated into the Kaumera network is assumed to be embedded into the polymeric chains of the proteins and polysaccharides it contains. Kaumera contains both positively and negatively charged groups (among other carboxylates and ammonium groups), therefore the charge of the surface of Kaumera agglomerates can change from negative to positive based on the conditions and orientation of the chains. Thus, the pH can play a role in the strength of the network. Two factors have been examined in the following measurements, the effect of pH on the yield stress and the effect of the Kaumera charge that has been used.

The positively charged Kaumera has been prepared by the PhD researcher Suellen Pereira Espindola (ChemE/Advanced Soft Matter). Kaumera with positive surface charge can be obtained with an initial purification step at basic conditions and heating, followed by a separation step and reacidification of the soluble fraction. The final concentration of solids is

2.33% w/w, and the positive surface charge has been confirmed with zeta potential measurements made by the researcher. For simplicity, this suspension has been named as positively charged Kaumera (+Kaumera).

On the contrary, the acidic Kaumera suspension from Zutphen has been named negatively charged Kaumera as the zeta potential measurements suggest (-Kaumera). Samples were made with both +Kaumera and -Kaumera after mixing them with XG at pH4 and pH7. The yield stress has been obtained by fitting the rheological data to the Bingham model.

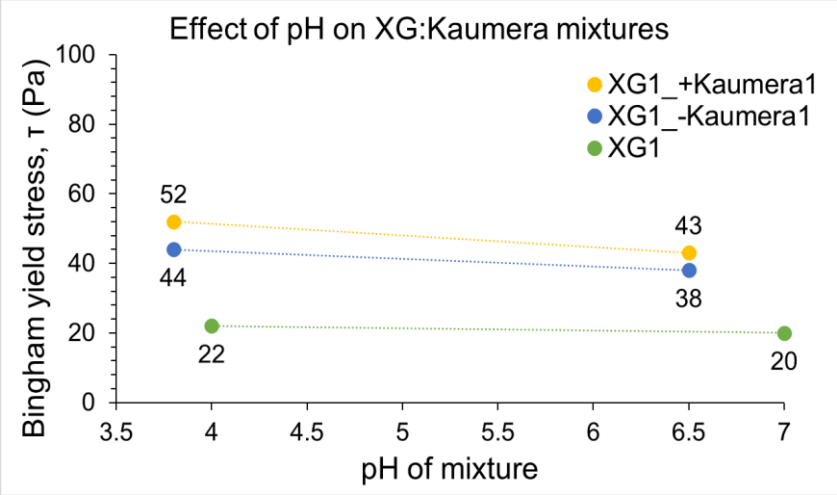


Figure 9.8: Yield stress of 1:1 XG/Kaumera samples as function of the pH of the final mixture

The combination of +Kaumera with Xanthan gum at PH 4 exhibit slightly higher yield stress than the similar pH mixtures with -Kaumera. This enhanced properties at pH 4 can be partially attributed to the pKa of the active groups in xanthan gum and in the Kaumera network. From literature it is known that the carboxylic groups of xanthan gum have a pKa of 4.6. (Bueno & Petri, 2014), whereas the Kaumera network is estimated to have a value close to 4 (Communication S.P Espindola on 17/02/22). The mechanism that could explain this behavior is possible stabilization of the Kaumera and XG chains through hydrogen bonds, as those are sensitive to changes in surface charge. At this pH, it is estimated that the two networks have a more open structure and can easier diffuse into each other to create a combined network.

In neutral conditions (pH6.5) the rheological properties are weaker in comparison to pH4, as the charge balance on the active groups of XG and Kaumera is altered and combining the two networks becomes more challenging.

The +Kaumera still seems to yield slightly stronger gels than the -Kaumera. The yield stress of the xanthan gum network alone is not affected by the pH change. Therefore, the higher yield stress values are associated with the stronger interaction between the chains at pH close to the pKa of the active groups.

Chapter 10: Conclusions

Taking a critical view on the results presented in this report, the use of a gel barrier as an effective way to reduce sedimentation in the Rotterdam port area require further development before it can be implemented. The main conclusions that are made concern the **technoeconomic feasibility** of the gel product, **application strategies**, and **environmental considerations** that can be used to create a strategic road map for further product development.

10.1. Gel recipe

The gel stiffness of the final product can be tuned by adjusting the concentration of solids and gelation agent in the final recipe. Gels with shear stress from 80-5,000 Pa can possibly be developed by mixing mud from port of Rotterdam with a gelation ingredient.

- The appearance of the gels can range from liquid to very stiff pastes and is related to the shear stress that the sample exhibits at specific shear rate

It is technically feasible to mix PoR mud with xanthan gum, guar gum or CMC in relatively small concentrations (1-3% w/w) and create gel products with sufficient density to avoid flotation (1.2g/ml) and stiffness to preserve its shape (250Pa).

- For XG, same rheological properties can be achieved either with a high amount of solids and small amount of gelation agent or by increasing the concentration of polymer and adding less solids in the mixture. Both XG3Mud10 and XG1Mud20 samples have a yield stress of 250Pa.
- A higher concentration of CMC (5%w/w) is required to achieve the desired shear stress in comparison to XG.
- CMC gels dissolve in a few hours underwater and thus CMC at the current degree of polymerization is not an appropriate agent for an underwater barrier.
- Based on literature review, gelation ingredients that require heating (starch) or are expensive (alginates, chitosan) were rejected as the gelation agent for the final product. Their use would result in high material and manufacturing cost.
- Polyacrylic acid (PAA) despite being a good agent for gelation, is not recommended for the use in the barrier because of its slow degradation rate which can have environmental implications**.**
- Kaumera with the current low concentration of solids does not provide sufficient strength to build a barrier. A more appropriate application would be as an eco-friendly flocculent as it is seen that dried Kaumera can increase flocculation rates in diluted clay suspensions.

The material cost of a solid gel barrier was estimated for various gelation agents. The use of xanthan gum, guar gum and polyacrylic acid as a gelation of agent in a solid gel barrier result in the lowest material costs for each m^3 of the final product. CMC is also a feasible option but cannot provide the same underwater stability as xanthan gum.

Therefore, xanthan gum was selected as a gelation agent in the recipe. The use of this ecofriendly polymer is typical not only in the food industry but also in structural operations as a

stabilization agent in soil for dyke support and in drilling fluids as a rheology modifier. Hence, it is readily available to be used for large scale projects.

For the same concentration of solids content, Ilite and pottery clay mixed with polymers result in less strong gels than mud. This could be related to the presence of organic content in the sediment in Botlek and potentially to different particle size. Mud recovered from sedimentation traps of port of Rotterdam is, thus, an important ingredient in the final recipe of the gel as it provides the desired strength at minimal cost.

- The particle size of the solids contained in the barrier will affect its stiffness. The smaller the particles the stronger is the gel that is made.
- The combination of XG and GG in ratio 1:1 results in slightly higher rheological gel properties than pure XG or GG gels.
- Gels with 1%w/w salt concentrations exhibit slightly stronger rheological properties than gels without the added salt.
- The addition of 2.5% salt in XG1Mud10 gels increases significantly the rheological properties. For XG1Mud10 mixture the yield stress with added 2.5% NaCl salt is around 300 Pa after equilibration. This is roughly an increase of 3 times in comparison to the original gel without added salt. This can indicate that after a curing time of a few days, the Na^+ ions can stabilize the polymeric chains and clay particles possibly by coiling the polymeric chains while binding to clay particles in the structure.
- At very high NaCl concentration (25%w/w) there is no strengthening effect. This could be explained by the rapid screening of the charges on the polymeric backbones which hinder further interactions with the particles.

Hence, the trials made with added NaCl salt in XG/Mud gel mixtures indicate that there is an optimum ratio of added salt and XG content that can result in stiffer gels. The content of salt already present in the mud samples is not known, however from the salinity profile in Botlek can be speculated that contains possibly another 2-3% w/w of NaCl. Therefore, the composition of this a gel with added 2.5% salt might be closer to XG/Mud/NaCl = 1:8:5 of dry weight.

In a similar way the addition of divalent cations, such as Ca^{2+} is expected to also have a strengthening effect on the gels possibly after a longer equilibration period. A systematic investigation for the curing time has not been performed during this IDP project, however it is worth investigating further, as the bigger cations with higher charge can bring the polymeric chains closer together.

High salt concentration seems to provide a strengthening effect on the gels, however, the behavior underwater has not been evaluated. The water intake due to osmotic effects will also play a role in the swelling degree of the barrier. Therefore, a detailed investigation is required to determine the salinity that the gel recipe needs to have to provide sufficient strength and low enough swelling rate to ensure longer product lifetime.

10.2. Underwater stability study for base recipe

The technical feasibility of a barrier was proven experimentally by performing lab scale underwater trials in 2.5%w/w NaCl water.

- Even though the tested gels swell underwater by 120% of their initial volume (scale 200g) this is expected to be lowered at bigger scale.
- Smaller gels (150g) tend to swell more expanding up to 200% of its original volume), which suggests that the ratio of surface area and volume can influence the water intake and swelling degree.
- The salinity of the water and the salt concentration in the barrier need to be carefully tuned with the conditions in the barrier location. Osmosis plays an important role in the swelling degree of the barrier.
- Once the gel has reached its maximum volume, xanthan gum diffuses faster out of the barrier. As a result, mud particles are no longer bonded to the system and the density of the barrier decreases over time.
- The density in the core of the barrier is rather stable for longer time as the solid particles cannot diffuse out of the system.
- The rheological properties deteriorate as a function of the distance from the core of the barrier and over time.

Visual observation tests on erosion of the gels show that the barrier should be built in small channel in Rotterdam port area where the speed of currents remain below 0.1 m/s. The gels already after the 1st week underwater, they start eroding at water stream injections of 0.2m/s. It is expected that the barrier will be preserved on such locations for 3-4 weeks.

The suggested mechanism includes:

- Water intake of the xanthan gum network and expansion
- Faster diffusion of XG once maximum hydration has been achieved
- Mud particles from the barrier's surface are no longer contained in the gel system
- Density in the core remains rather stable as the solids are restricted by surrounding gel
- The barrier gradually deforms as the strength of the network decreases.
- The barrier flattens out due to gravity

10.3. Gel lifetime and efficiency in mud reduction

Besides the material cost, the effectiveness of the barrier in reducing the incoming mud in the port area and the frequency of placing the gel in the port are critical parameters that will affect the economic feasibility of the barrier.

For the gel barrier project to be economically feasible the frequency of the barrier and the material, manufacturing and placements costs need to be counterbalanced by the cost that is spared with the reduction of dredging operations.

- By making 1 barrier every 5 weeks in the Botlek entrance, 1 M€/y can be spared for every 45% mud reduction that the barrier can achieve on an annual basis. This means that the barrier needs to be stable enough to preserve its shape for 6 weeks and will

result in 45% less mud entering the port, thus reducing the amount of dredging operations by 45%.

- Even though, the current recipe can make a small barrier that lasts approximately 4 weeks, it is expected that a larger barrier can last longer. A swelling model for osmosis driven diffusion in large gel barriers is required.

Therefore, further enhancement and stabilization of the barrier will be required. To reach the desired target of 5% annual reduction of dredging costs in PoR, sedimentation control will be required in multiple areas in the port.

From trials made in a lab scale water tank it is shown that the barrier could potentially hinder partially the mud, however as an estimation more than 50% reduction is highly unlikely to be feasible in real conditions in the port. Hence, the lifetime of the barrier should be further prolonged to 10-12 weeks.

10.4. Application strategy

The main conclusions for the application strategy are drafted after comparing the material, manufacturing, and transportation cost of the various concepts against defined criteria from a case study. Three concepts have been evaluated, the batch preparation, the in-line application approach and the concept of the premade gel barrier. With respect to the time required for applying the product, a barrier in the port can be made with all concepts within 4 hours. The total cost related to manufacturing alone are significantly lower for all three strategies (0.72 €/m^3 of barrier) than a typical dredging trip with mud in a hopper dredger (2€/m^3 of mud). The energy of placing the barrier on location and cleaning the gel fragments at the end-of-life account for 90% of the total costs in the placement strategy.

However, material cost is the main cost driver in the project as a gel barrier with 1% XG costs approximately 0.1M€. It needs to be highlighted though that the dredged mud is a waste product that is constantly generated and removed from the port. Thus, by utilizing the end-of-waste framework this cost can be excluded from the overall cost estimation of the application strategy.

Finally, specifically for the unloading technique, the compatibility of each of the four discussed methods varies according to the gel structure and the accuracy on the applied location.

10.5. Environmental considerations

The battery limit for the CO_2 emissions calculation was the Rotterdam port area and nearby sites, thus CO_2 emissions for extracting XG powder from bacteria were not considered. The estimation includes emissions related to pretreatment, manufacturing, transportation and dredging during cleaning. The CO_2 footprint is higher if the emissions from the supplier are included.

The application method with the lowest generation of CO_2 emissions is the inline concept, where mud is dredged- mixed with xanthan gum and placed underwater in a continuous mode. This reduced the energy required for transportation and thus CO_2. At the end of its life the barrier can be reused to support dykes which can enhance the circularity of the product. Rebuilding the barrier on the same location is expected to still be possible even without prior barrier removal.

10.6. Kaumera

In this project, an investigation was made for utilizing Kaumera in Port applications. At the current stage the availability of Kaumera in acidic form and the relatively low solids-content are hindering the use of Kaumera as a gelation agent for the gel barrier application. Further research and development are needed to achieve better gelation properties. However, through an investigation of the rheological properties of Kaumera at various conditions of concentration, pH and cation interactions, development directions can be provided towards using Kaumera initially as a flocculation agent. The main conclusions include:

- Thermal drying of Kaumera suspension significantly deteriorated the rheological properties of the mixture. The yield stress dropped by 1 order of magnitude at 60^{o}C and 3 orders of magnitude after drying at 105^{o}C.
- Rewetted dried Kaumera 105^{o}C powder is better for flocculation than the original suspension.
- When Kaumera suspensions are combined with clay particles the observed strength of the mixtures increases with increased concentration of the solid Kaumera content.
- The highest relative increase of yield stress has been observed for 1:1 mass ratio between clay particles and dried Kaumera 60^{o}C, where the final network is 2000 times stronger than the initial strength of the clay suspension. Whereas, for higher ratio 2:1 the rheological properties increased roughly around 120 times.
- For the tested system, 30% increase of the rheological properties is expected when clay is combined with basic Kaumera over the acidic form
- Slightly stiffer gels have been obtained when Kaumera is combined with Xanthan gum at pH4 instead of pH7
- Dispersing acidic Kaumera in deionized water at low shear, results in small Kaumera agglomerates with a size of about 30µm.
- The overall charge on the surface of these irregular-shaped H-Kaumera agglomerates is negative, based on zeta potential measurements.
- The addition of Ca^{2+} shows a reduction in the recorded particle count on the zeta potential measurements, which indicates that flocculation occurs in the sample.
- The calcium cation addition shows a time-dependent effect on the zeta potential, however, because of flocculation this behavior could be attributed to the unflocculated particles with higher charge that remain in suspension.
- Flocculation seems to occur between the Kaumera particles with added [Ca^{2+}].

These initial observations cannot answer all questions about the complex Kaumera system; however, they provide an indication of strong interactions between Ca^{2+} and Kaumera, which could act as a flocculant.

Chapter 11. Recommendations

To assist in further development of the gel barrier idea, recommendations for future research are presented in this section. These refer to improvements that can be made for the gel recipe, cost estimation for the application strategy and CO_2 emissions. A road map for future development steps will also be discussed. Finally, more recommendations for the development of Kaumera are included at the end of the chapter.

11.1. Improvements in gel stability

The main trade-off observed in the recipe is related to the lifetime of the barrier and the biodegradability rate. As shown in the sensitivity study, for a given reduction in mud, higher cost savings can be achieved when less barriers are required. Thus, it is critical to increase the lifetime of the gel, ideally to 6 months-1 year. The following suggestions can result in stronger networks, possibly with less swelling and longer lifetime:

- Investigate the effect of [Ca^{2+}] in the stability of the gel barrier underwater. Define the optimal concentration for minimal swelling. Indicators similar to those used in EDTA titrations could be used to visually study the diffusion of free calcium cations from the gel into surrounding water.
- Recipes with even less amount of xanthan gum (0.5%w/w) can be possible if clay or other high-density particles are added to the gel. This will provide the required strength but will lower the material cost.
- Detailed study of the effect of curing time and NaCl concentration in the yield stress of the gel. Gels made with salt 2.5% seem to have a longer equilibration time and their rheological properties are enhanced significantly after a few days from manufacturing.
- Tune the swelling rate of the barrier with the tidal effect in the port. The changes in water salinity related to the tide can affect the water intake in the gel. In fresh water the barrier wants to swell whereas in saline conditions the gel can shrink.

The composition of mud is not constant in every area of the port. Variations in organic content, in particle size and degree of consolidation can possibly affect the strength of the final gel product. Therefore, a protocol needs to be implemented in which a small-scale trial validation trial take place in the lab before the use of mud from a different location. The following should be defined prior to use:

- Content of dry solids in the mud sample
- Conductivity
- Organic/ inorganic content
- Particle size and dominant clay types
- Isoelectric point of the dominant clay particles in the mud

The trials of preliminary gels show that XG systems might be a good candidate for other applications:

- Low density XG gels float in water and could potentially be used for oil-spill control.
- Utilizing XG/Mug gels for stopping temporarily leakage in small pipes might be possible as the gels with XG and mud start to swell after they come in contact with water.

- XG seems to bind well with divalent heavy metals and aluminium. Therefore, the barrier could be collected at the end of its life and reinforced with xanthan gum and be used to clean contaminated sediment rom heavy metals.

Finally, with respect to the use of other gelation agents, polyacrylates could potentially substitute xanthan gum in the formulation provided that their biodegradability rate can be increased. It is recommended to develop faster biodegradable polyacrylic acid by modifying its monomers. This alternative polymer might increase the lifetime of the barrier while providing an eco-friendly solution at low cost.

Stability with movement

Both liquid and stiff gels are affected by the water movement. The stability of these two types of products with movement can also be studied with the use of the rotating wheel device that is available in the shared lab of Deltares and TU Delft. This device can rock from side to side by following a sinusoidal movement. For fluid gels, the interface interaction between the gel and water surface can be visually studied. For stiff barriers with the use of the wheel it can be studied how stable the barrier is and if it falls over or loses its shape when moved. An overview of the setup can be found in Figure 11.1.

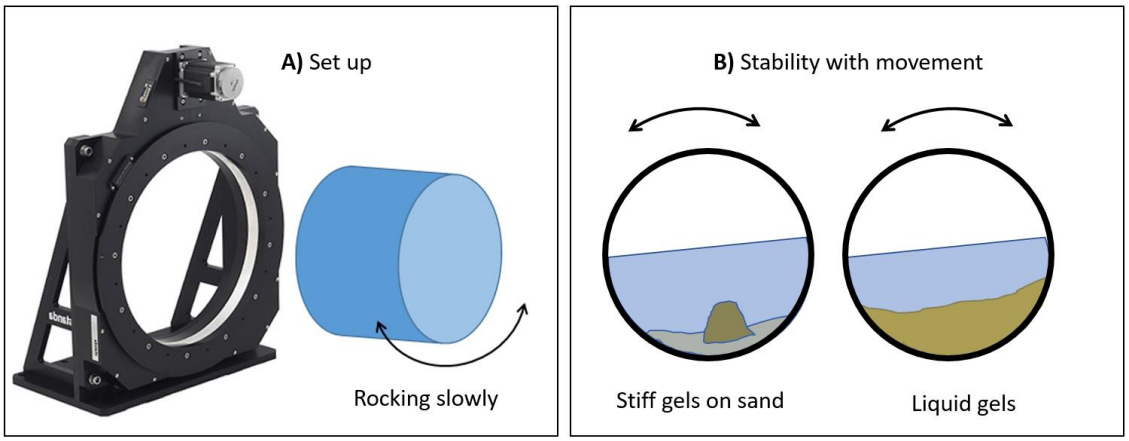


Figure 11.1: A) rotation wheel device, b) Simulation of movement for fluid and stiff gels

11.2. Improvements for Application strategy

In this paragraph some additional considerations are discussed with respect to the application on site and manufacturing of the gel product. **Another** option to be considered as **an application strategy** is to directly mix and **create the gel underwater**.

- A sedimentation trap could be one possible location to inject a concentrated solution of xanthan gum and mix with mud underwater.
- Some mixtures with bentonite and polyethylene glycol can be converted instantly into a gel by rapid shaking or injection (Mar Ramos-Tejada & Luckham, 2015). It is worth studying if a similar effect could be achieved with XG as this will ease the application process

The density of xanthan gum solution is, however, very low at the moment as air is incorporated in the mixture during preparation and the polymeric solution is floating. Therefore, density adjustments are required, possibly with the addition of insoluble particles. Calcium carbonate added clays or grout all have high densities and at small concentrations could be a starting point for this investigation. In this case it is critical to evaluate if the gel will remain navigable for ships. Otherwise, the barrier needs to be placed in locations where large ships do not pass frequently.

Cost estimation

Transportation of products in smaller channels in the port seems to be accompanied by higher costs than the base case as found in literature (Van der Meulen et al., 2020). According to the given cost estimates, transferring the product for the same distance in the smaller waterways should be increased by a factor of 2. Once more details are available (barrier volume, location, contracting companies, equipment to be utilized) it is recommended to conduct a more detailed cost analysis by considering the following:

- Redefine a base case by breaking down the costs for each action (dredging, transportation, sailing back, etc.).
- Add a correction factor to account for the differences in fuel consumption and capacity of the different size vessels in the port.
- Account for extra costs related to waiting times, renting and man-hours for additional operations, as they can dramatically increase the total cost.

The evaluation matrices presented in this report focus specifically on the gel barrier approach with some consideration of the other gel structures. This overview is meant to assist in the future development of a gel product idea and is not designed to provide detailed cost estimations. More years of development are required before a gel product will be used for sedimentation control in the port. Therefore, it is suggested to use these considerations as a starting point for detailed calculations once the final recipe and function of the product has been clearly defined.

With respect to the use of raw materials for the barrier, the environmental impact of producing and importing xanthan gum should also be assessed. Depending on the scale of the gel products that will be used in the Rotterdam port areas, it is recommended to assess the economic feasibility of xanthan gum production in bioreactors on nearby sites.

11.3. Roadmap

A road map with the key activities has also been made to connect the preliminary findings of this IDP work with the ongoing CFD study and suggest potential actions from prototyping to pilot scale trials in the port of Rotterdam. The key steps of the road map have been identified and are presented schematically in Figure 11.2.

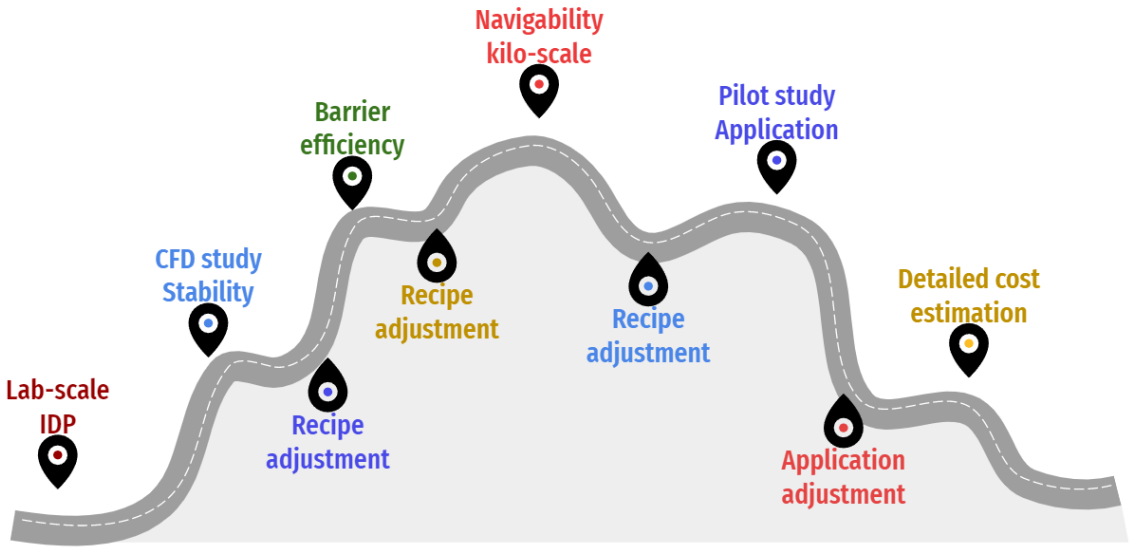


Figure 11.2: Milestones in the development of a gel barrier in Rotterdam port area

Can the gel barrier stay in place?

As part of the second project phase of this project, a CFD study has started to investigate under which conditions the barrier can stay in place. Focus has been given on the mechanism of erosion for this viscoelastic barrier to properly monitor how stable it can be with the currents movement in the port. It is recommended to check whether the density of the barrier is sufficient for it to remain on the desired location and proceed with recipe modifications (rheological characteristics, solids content) if necessary. Consideration of the shape of the barrier should also be provided at the end of the study to avoid tumbling of the barrier with the water currents. Possible locations for the barrier should be proposed based on the hydrodynamic conditions.

What is the barrier's efficiency in mud reduction?

As a proof of concept, kilo scale experiments could take place in the flume tank in Deltares. A barrier of 5-10Kg with the optimized density and strength could be made and placed under constant circulation of water to show first the stability over time. The ability of the barrier to partially block suspended mud particles can be evaluated in these trials under various flow conditions. The output of these trials should also provide an indication of the lifetime that the gel should have to contribute to reduction of overall dredging costs in the port.

Can ships navigate through the barrier?

It is also critical to investigate how the gel will affect current ship navigation routes in the port. Ideally the barrier should not obstruct any operation, however if large ships are passing close to the barrier, their propeller could generate much higher shear and destroy the structure. Hence, building the barrier must be fitted around arrival and departure of large ships in the barrier location. A CFD study or a flume experiment could also indicate how the distance between the ship's hull and the barrier's top can affect the structural ability of the barrier.

Finally, even though the gel has a yield stress higher than the port navigable limits, it is expected that the shape of the barrier can be tuned to allow for ships to pass through. A thin wall barrier will be easily broken by a large vessel.

Go bigger - Pilot trial

Once the previous questions are answered the technical feasibility needs to be assessed at a larger scale. A quantity of 0.1-1 m^3 can be used to create a thin wall. A sedimentation trap in a small port channel in Pernis petroleumhaven could be a potential location for this test as it has lower speed of currents and is less busy that Maasvlakte or Botlek area. The application strategy can then be tested and adjusted based on the observations.

Combining different strategies

To achieve the desired reduction of dredging operation, maybe more than one techniques need to be combined in different areas in the Rotterdam port area.

- The barrier could also act as a medium to prevent density currents from salt intrusion.
- Using dried Kaumera as a flocculation agent in a sedimentation trap can also result in flocculation of mud which settle at faster rates, therefore allowing more mud to be collected into the trap. By placing slow-release bags of flocculent a constant powder release could result in controlled flocculation rates. However, for environmental reasons the bags or other containers used need to be properly fixed on the desired location underwater.

11.4. Kaumera development directions

During this project, promising results have been obtained for using Kaumera as a flocculant. Trials that were made in a parallel project, showed that rewetted dried Kaumera can be used as a bio-flocculant. For the Port, the use of Kaumera as flocculant could be used to stabilize mud is sediment traps, to prevent erosion and resuspension of this mud and lead to a faster and better dewatering of the slurry in the traps.

For high solids concentrations of Kaumera in the order of 10-20% w/w, gelation might be also feasible if a stable suspension can be made. Using Kaumera in gel barriers could specifically be of beneficial value for specific parts of the harbor, in combination with environmental requirements, such as development of aquatic life. As such, it is therefore expected that Kaumera gels could have a good potential in nutrient-depleted shallow water regions, where it would promote the development of underwater fauna and flora.

Hence, it is strongly recommended to increase the solids content in Kaumera suspensions to achieve sufficient concentration for gelation. Using heat (60^{o}C) to produce dry Kaumera can significantly alter the structure of the Kaumera network and alter the rheological strength of the final product. Thus, some alternatives are suggested for increasing the concentration obtained in the last process step of the Kaumera production.

- One way to achieve higher concentrations is by designing a more effective centrifugation system.
- Another way would be to incorporate industrially available drying techniques for heat-sensitive materials, like spray drying to obtain a dry product without compromising the rheological properties.
- Freeze drying could also be applied at lab scale but the operation cost for industrial size batches is high.
- Improving the yield of the sludge extraction and purification process can increase the mass of obtained product.
- By increasing the number and capacity of the manufacturing sites, based on economies of scale, the selling price of the final product can also be further reduced.
- Manufacturing dry Kaumera can also increase the lifetime of the product as microbial growth occurs much slower at dry conditions. Addition of an antimicrobial agent, such as sodium percarbonate can also be beneficial in reducing the microbial count in the Kaumera sample.

Additionally, with respect to the charge of Kaumera used, it is suggested to focus more on stabilizing the production of a high pH solution or positively charged acidic Kaumera suspension than producing the less active negatively charged Kaumera at low pH. Basic Kaumera is soluble and readily available to react with polymeric systems and interact with clay particles. Thus, it is also recommended to investigate the exchange reaction kinetics with $CaCl_2$ and basic Na-Kaumera. The stoichiometry of this reaction can be better estimated in comparison to the acidic Kaumera. The reaction could possibly be described with the following equation:

$$2\text{Na-Kaumera} + CaCl_2 \rightarrow 2NaCl + \text{Ca-(Kaumera)}_2$$

Because of the positive and negative charges on the Kaumera chains, increased salt concentration might also result in swelling of the Kaumera gels, as the conformation of the structure changes. Perhaps swelling will occur because of the osmotic effect, but crystallization of some regions might also take place which can potentially provide more stability.

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Appendix A: Estimation of specifications and assumptions

A1. Gelation agents

Different gelation agents that are commercially available were considered as a possible ingredient in the final gel product. Eco-friendly materials were evaluated (Table A1) as the final product will need to comply with environmental regulations. Some like xanthan gum, guar gum, starch and gelatin are commonly used in the food industry, whereas others like alginates and chitosan are excellent gelation compounds that are widely used in bio applications.

Table A1: Evaluation of various gelation agents

Specification	Gelation time (min)	Gelation point %w/w	Viscosity at 1% w/w	Dissolution temperature (°C)	Shear for Mixing	MW M Da	degradation (%w/w/y)	Cost USD/ Kg
Xanthan gum	0.5	>0.1	3000	<25	High	2-20	100 in 1w	1.5-3
Guar Gum	3-5	>0.1	3000	<25	High	0.05- 8	100	2-3.5
CMC	5- 7.5	>1	800	<25	High	0.09-0.25	95% in 10w	0.9-2.3
Starch	3	<1	2	55-85	low	50-80	100	0.5-1.5
PG starch	unk	<1	1000	<25	low	0.07	100	0.5-1.5
Polyacrylate	2-5	<1	>2000	<25	High	0.13-1.25	1-9	2
Chitosan	4	<1	300	25 in Acid	High	0.05-0.19	85% in months	8-30
Na Alginate	6-30	1.5	700	<25	High	0.12-0.19	100	8-20
Gelatin	40	>0.5	2	35-40	Low	0.4- 50	100	1-5
Target	<5	<5	>1000	10	<Medium	>1	50	<5

From the above candidates, it can be concluded that XG, GG and CMC are potentially good ingredients that can be applied in an underwater gel barrier. The properties shown on table A1 were created based on the following sources (Table A2).

Table A2: List of Literature for polymers

Polymer	**Source**
Starch	(Reddy & Bhotmange, 2014), (Alibaba, 2021a), (Lund, 1984) Pregelatinized: (Hedayati et al., 2016), (Alibaba, 2021b)
PAA	(Sigma Aldrich, 2021c), (Alibaba, 2021)
CMC	(Indiamart, 2021), (Kundu & Banerjee, 2019), (Benslimane et al., 2016).
Chitosan	(Sigma Aldrich, 2021b), (Wen Wang & Hsiung hon, 2005), (Tolano-Villaverde et al., 2016).
Sodium Alginate	(Sigma Aldrich, 2021a), (Alibaba, 2021c), (Shaikh et al., 2014)

Polyacrylic acid is a commonly used polymer that is used in many everyday items, like toothpastes for its mucoadhesive properties and in disposable diapers due to its ability to absorb water. Additionally, polyacrylic compounds have been used as a coating for fertilizers in the agriculture industry. The ecotoxicological effects of PAA in soil and its release to water body have been reviewed by (Gilda Dell'Ambrogio & Wong, 2019). As reported by the authors, currently the use of such coatings is not permitted in Switzerland because of environmental concerns. A summary of the biodegradability rates of polyacrylic acid that is discussed in this review is provided in Table A3.

Table A3: Reported degradation rate of PAA in literature

Polymer	Degradation rate	Time	Conditions	Source
PAA	5.9%	16 months	Compost, 0_2	(Stegmann et al., 1993)
PAA	Up to 0.24%	6 months	Soil	(Wilske et al., 2014)
PAA coating	1.77%	12 months	Soil	(Liang et al., 2018)
PAA coating	1.69%	12 months	Soil	(Liang et al., 2019)
PAA	1-9%	Per year	Soil	(Hüttermann et al., 2009)

The degradation rates that are reported in the Table A3 above appear to be relative slow considering that the intended application site will in a water body with connection to sea and river water. An investigation of the degradation rates of PAA in the conditions of PoR will be required before applying this ingredient in the barrier. Therefore, the use of PAA is not recommended for the gel barrier project. However, it is recommended to develop PAA that biodegrades at a faster rate. Investigating the environmental impact of polyacrylates in the Rotterdam port area is also a suggestion for future research.

For the gelation agents that are presented in the economic evaluation (Chapter 7) the selected concentration when taken from literature when experimental values were not available. The values and sources are presented in Table A4.

Table A4: Gel stiffness for various agents and concentration obtained from literature

Gelation agent	Concentration (%w/w)	Yield stress (Pa)	Comments	Source
Sodium Alginate	2.0	60-80	from graph	(Gladukh & Podorozhna, 2021).
Polyacrylic acid	2.5	120-200	from graph	(Gupta, 2018)
Chitosan	3.0	100	For hydrogel with 1.8% Acetic acid	(Szymańska et al., 2015)
Pregelatinized Starch	4.0	60	Based on Corn starch	(Ansharullah et al., 2020)

A2. Gel stiffness per concept

The gel stiffness for the different concept ideas will depend on the function that the gel product needs to perform, the stability overtime and the environmental conditions that are present to the application area. The Liquid gels product need to have a shear stress lower than the upper navigation limit of 80 Pa that currently is considered in the port. For the stiff gels the strength needs to be higher so they can maintain the desired shape and are dense enough that they cannot be carried away but water currents and passing ships. The target values for each application were determined based on the lab experiments with xanthan gum and mud particles (Results on Table A5)

Table A5: Shear stress target for the various concepts

Application	**Desired Shear stress (Pa)**
1) High-density gel barrier	200
2) Gel slope in terminals	500
3) Dry dock gel barriers	300
4) Liquid gel in access channel	80
5) Liquid gel in small port channels	50
6) Gel in sedimentation trap	500

A3. Gel lifetime per concept

Each one of the six concepts that are presented in Appendix B, will have different lifetime expectancy. A simplified break-even analysis took place to find the lifetime that the gel needs to have to provide the maximum annual profit. The analysis includes only the material cost per year to create the product and not the manufacturing cost (Results in Table A6).

Table A6: Estimation of lifetime of gel products per concept

	1	2	3	4	5	6
	Gel barrier	Slope barrier	Gel in docks	Gel in access channel	Gel in PHaven	Sediment traps
Lifetime (y)	**Annual savings with gel (M€/y)**					
0.05	0.0	-4.3	-9.1	-97.8	-324.9	-3.2
0.08	0.9	0.0	-3.2	-57.7	-191.3	-0.6
0.10	1.1	1.0	-1.9	-48.8	-161.6	0.0
0.14	1.4	2.4	0.0	-35.5	-117.1	0.9
0.2	1.7	3.7	1.8	-23.6	-77.4	1.7
0.5	2.1	5.2	3.9	-8.7	-27.9	2.7
1.0	2.2	5.8	4.7	-3.8	-11.4	3.0
2.0	2.2	6.0	5.0	-1.3	-3.2	3.2
3.3	2.3	6.1	5.2	-0.3	0.0	3.3
4.0	2.3	6.2	5.2	0.0	1.0	3.3
10.0	2.3	6.2	5.3	0.7	3.5	3.3
20.0	2.3	6.3	5.4	1.0	4.3	3.3
100.0	2.3	6.3	5.4	1.2	4.9	3.4

From the analysis above it can be concluded that the annual savings will reach a maximum since the annual savings from dredging are fixed, whereas the annual material cost will be reduced

with the increasing gel lifetime. The point when the savings per year reach a plateau, were selected as the optimal lifetime of the gel barrier and are highlighted in the Table A6 above.

A4. Estimation of annual savings per concept

Based on the model that is presented in Chapter 3, the annual cost savings were calculated for each one of the six concept ideas. The following assumptions were made:

Annual Dredging cost savings

The annual cost of dredging was calculated by multiplying the following factors:

Dredging Savings= Annual dredged volume** x **Dredging unit cost** x **% of volume reduction

The dredged volume refers to the amount of sediment that is expected to be collected from the area where the gel product is applied. For example, the 3rd concept is going to be placed in terminals that are present in Maasvlakte, Europort, Botlek and Pernis. Therefore, the sum of the volumes in these 4 areas is the total annual dredged volume. The unit cost of dredging will be different from location to location as it was explained in chapter 3.

The percentage of reduction is based on the sensitivity analysis for the gel barrier concept, however the other ideas are not investigated in details, thus the % reduction is an estimation. For example, by replacing the water body of one of the petroleum ports in Pernis, there mud particles will not be able to enter the port and thus sedimentation will be 100% prevented. Other concepts are expected to have% smaller reduction in sedimentation rates as they cannot eliminate the sediment but rather hinter its spread.

Annual Material cost

The annual material cost was calculated by multiplying the following factors:

Annual Material cost= Gel volume** x **Frequency** x **unit Cost of gel x Gel % content

The gel volume was estimated based on the details provided for the concepts in Appendix B and the frequency of gel placement was estimated in section A3 of this appendix. The summary of all calculations is presented in Table A7 below.

Two more assumptions were made with respect to the content of the gelation ingredient

- For the liquid gel barriers, it was assumed that they consist of 0.5% w/w gelation agent with low unit cost (Such as xanthan gum) and thus the material cost was estimated to be 11€/m^3.
- For 1% w/w of gelation agent a stiffer gel can be made when mud is added in the formulation and the cost used for the estimations is 22 €/m^3.

Table A7: Estimation of annual **material** gel cost

Concept / Location	Cpolymer %w/w	Frequency	Material cost of gel M€/y
1) Gel barrier	1	10 times/y	0.1
2) Slope barrier	1	1 time/y	0.5
3) Gel in Dry docks	1	Every 2 y	0.4
4) Gel in access channel	0.5	Every 10 y	0.5
5) Gel in P.haven	0.5	Every 20 y	0.8
6) Gel in Sedimentation traps	0.5	2 times/y	0.7

Annual Savings

Finally, the Annual savings are calculated by subtracting the annual material cost from the annual dredging savings. In the case of a gel barrier the manufacturing and application cost was also included in the calculation. However, for the other concepts only the material cost was used as the application strategy needs to be specifically designed for every gel structure. The results for the concept ideas are provided in Table A8. It is worth mentioning that seasonal variation in the incoming particulate matter were not considered in this comparison as the main purpose is a rough estimation and not a detailed calculation.

Table A8: Estimation of savings on dredging cost per concept

Concept / Location	Dredged Volume In gel location Mm3/y	Annual volume Dredging Reduction, %/y	Annual material cost, M€/y	Annual % cost savings
1) Gel barrier	2.0	-45%	0.1*	22%
2) Slope barrier	9.0	-30%	0.5	27%
3) Gel in Dry docks	6.0	-60%	0.4	56%
4) Gel in access channel	1.0	-80%	0.5	47%
5) Gel in P.haven	2.8	-100%	0.8	84%
6) Gel in Sediment traps	4.0	-80%	0.7	64%

*Including manufacturing, transport, application, and cleaning costs.

A5. Composition details for gel barrier

For the application cost estimation of the gel barrier product (Batch, in line, premade) a gel recipe was defined to be able to compare between the concepts. It was assumed that the barrier will be made by combining xanthan gum and dredged mud, based on the recipe of XG1Mud20. The characteristics of the gel barrier are presented in Table A9.

Table A9: Gel barrier recipe and characteristic used for calculations in the application concepts

Gel barrier characteristics	Metric	Value	Details
Concentration of xanthan gum	% w/w	1	Dry mass in gel barrier
Concentration of mud	% w/w	20	Dry solids in gel barrier
Yield stress	Pa	250	Same in XG1Mud20 gels
Volume of gel barrier	m^3	5,500	Trapezium (bottom 100- top 75m) x (width) 40m x (height) 1.5 m
Barrier density	t/m^3	1.15	Based on lab tests
Total weight of barrier	t	6,325	Calculation
Weight of dry XG powder	t	63	For manufacturing in concept 2
Weight of 3% XG solution	t	2,108	Contains 63t of dry XG
Density of 3% XG solution	t/m^3	1.01	Based on lab trials
Volume of 3% XG solution	m^3	2,087	For manufacturing in concept 1,3
Weight of dredged mud*	t	4,217	Assuming 30% solids content
Density of dredged mud	t/m^3	1.24	Assuming 30% solids content
Volume of dredged mud	m^3	3,413	For manufacturing concept 1,2,3

A6. Time and dredging cost- Base case

A base case was drafted **to estimate the target** values of the specifications in the application strategy. In this way the various concept application ideas can be compared and evaluated in a common matrix. The base case describes the time and costs involved for transporting 5,000 m^3 dredged mud (density 1.2Kg/m^3) from Botlek to the North Sea. The Table A10 gives an overview of the characteristics for the base case.

Table A10: Time requirements and cost details in **base case**.

Characteristics of Base case	Units	Value
Quantity of dredged mud	m^3	5,000
Transportation distance (round trip)	Km	58.00
Transportation time	H	3.03
Dredging time	H	0.85
Discharging time	H	0.07
Total time	**H**	**3.95**
Total cost	**€**	**10,000**

By analyzing the time required for each step the unit cost of dredging alone can be estimated that the transportation cost is roughly 80% of the total and the dredging around 20%. Thus:

Transportation cost = 0.028 €/Km/m^3 and **dredging cost = 0.4€/m^3**

Similarly, the total time of manufacturing, the gel and applying to the desired location needs to be comparable to the overall time of the base case, roughly 4h per barrier.

Target: **Total time of a gel barrier** < Overall time of base case (**4h**)

A7. Transportation and unloading cost

According to literature transportation of material via the waterway of Rotterdam is influenced by many factors, as for example the size of the vessel used, the sailing velocity and the energy consumption of the engine. The calculations for the intermediate application concepts were made based on the transport cost values provided from the KiM (kenninstutuut voor Mobiliteisbeleid)(Van der Meulen et al., 2020) for the year 2018. These refer to large ships with a capacity of up to 3,300 t (or 2,750 m^3) and are:

- 3.29€/km for containers transferred on large vessels
- 3.17 €/km for bulk transport of materials with a large vessel

With the above information it is suggested that containers cost 1.04 more times to be transported than bulk material. Also, we can conclude that based on these data, a round trip of 58km would result in roughly in 200 € for 2,750 m^3 of mud or transport cost of 0.07 €/Km/m^3 $_{of\ gel\ barrier}$. Since this cost is double than the cost defined previously in the base case 0.034 €/Km/m^3 $_{of\ gel\ barrier}$, it is suggested that the base case cost is underestimated possibly by a factor of 2. Nevertheless, as the project is still in the very first stages of conceptual design it was decided to perform all calculations with the base case cost unit and apply a correction factor for the transportation of containers or bulk. As a recommendation, more detailed calculations can be performed in future studies, should the developments suggest that the gel barrier project is feasible.

With respect to the unloading cost, in the base case the discharge can take place rapidly but in a less controlled manner. For estimating the concept performance, the unloading procedure was set to be the same in all concepts. The **assumptions made** include:

- Unloading time in 15min (for 5,500 m^3)
- With the use of a pipe for precise application with accuracy <2m
- Energy for unloading the barrier via pipe = Energy required for dredging 0.4 €/m^3

Appendix B: Estimations and Details of concept ideas

In this paragraph the six main concepts that were identified are explained in detail. The various estimations of the performance indicators are explained. Calculations and assumptions made are also included:

- Visualization of the gel product in each concept (not at scale)
- Details on how the product dimensions were estimated
- Volume of the gel product

B1. Concept 1: High-density gel barrier

One of the ideas that was initially proposed suggests the use of an underwater barrier that will reduce the spread of incoming mud particles into smaller port areas. The location of this barrier is expected to be next to the sedimentation trap in Botlek, based on the model presented on chapter 3.5 and the sensitivity analysis in chapter 7, the barrier needs to reduce the incoming SPM flow rate by 45% in the local area that is applied. The density of the barrier is assumed to be 1.2 Kg/m^3 and the total Volume ≈ 5,500 m^3 (trapezoid: 40m width, 1.5 tall, 100m base length, 75 m top length) whereas the material cost for such a barrier will be around 120 k€. A schematic of the gel barrier concept can be seen in Figure B1.

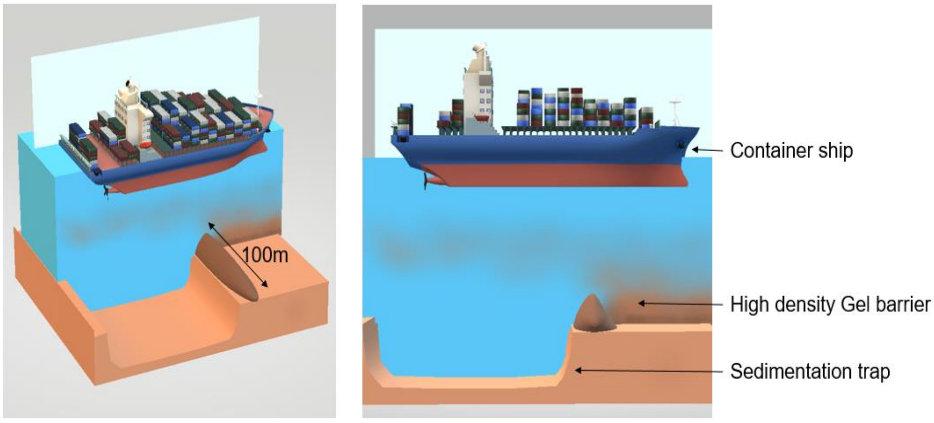


Figure B1: Gel barrier

B2. Concept 2: Slope gel barrier

The function of the gel slope barrier is to reduce SPM in difficult-to-dredge areas. The inclined barrier is attached to the wall and the suspended particles are being collected in the trap. The volume that needs to be dredged from the difficult areas in terminals is assumed to be reduced by 30%. Hence, dredging can be facilitated easier and is less expensive.

To estimate the size of the slope barrier, first it was determined what is the size of the ships in the area, based on the vessels that were anchored in Botlek area on 27/9/21. The Slope Gel will be a triangular base barrier with the following dimensions: L x W x H =240m x 40m x 5m. This will result in a gel volume of ≈ 24,000 m^3. Figure B2 shows a visual of concept 2.

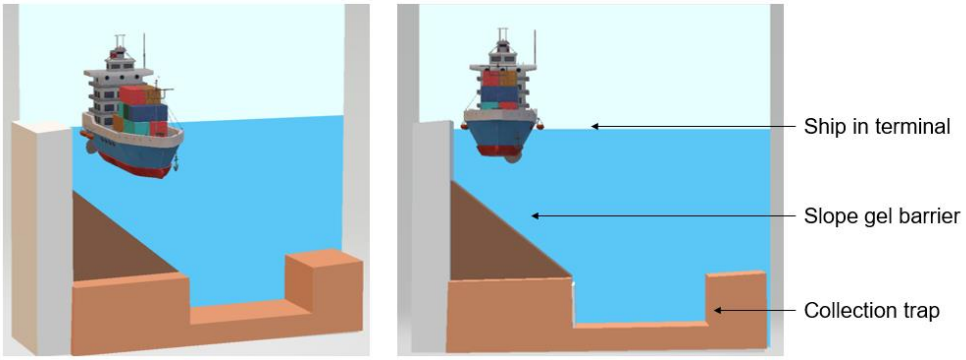


Figure B2: Gel slope barrier

B3. Concept 3: Gel barriers in Dry docks

Dry docks are specifically designed areas in the port where vessels can undergo maintenance. After the ship positions itself on top of the dry dock, the ship is lifted outside of the water and thus, it can be repaired. The maintenance can last up to several weeks or months. The area underneath the dry dock is prone to sedimentation, and during this repairment period sediment deposits gradually builds-up. Once the ship is ready to sail back the sediment prevents the dry dock from returning back to its original position, therefore dredging is required.

The use of a gel barrier will restrict the flow of mud particles while the dry dock is being used. Like the first concept idea, a stiff barrier can be place on each side of the dry dock. Two gels with trapezoid shape are used (dimensions: 40m width, 1.5 tall, 100m base length, 75 m top length) and the appearance of the gel in Figure B3. The gel volume for 2 barriers is ≈ 33,000 m^3 It is estimated that the barriers will reduce the dredged volume in this area by 60%. An alternative idea would be to construct the barrier in front of the dry dock door to prevent particles from entering the area.

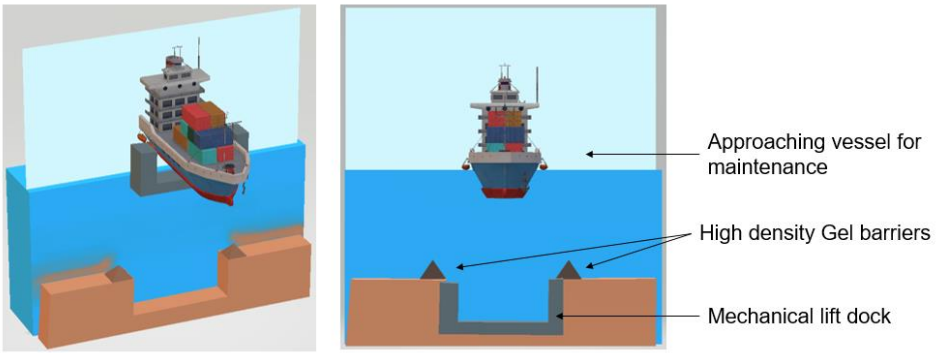


Figure B3: Gel barriers applied to dry docks

B4. Concept 4: Liquid gel in small port channels

This concept idea describes a liquid gel product that will substitute the water body on small port channels, like those located in petroleum haven in Pernis. The dimensions of a channel like this were estimated to be: L x W x D =500 x 150m x 20m. This will result in a gel volume around 1.5M m^3 and the materials cost for making a gel is estimated to be around 16.5 M€. If effective, this solution will prevent sedimentation 100% as particles cannot enter in the gel due to the difference in density. A view of this gel idea is shown in Figure B4.

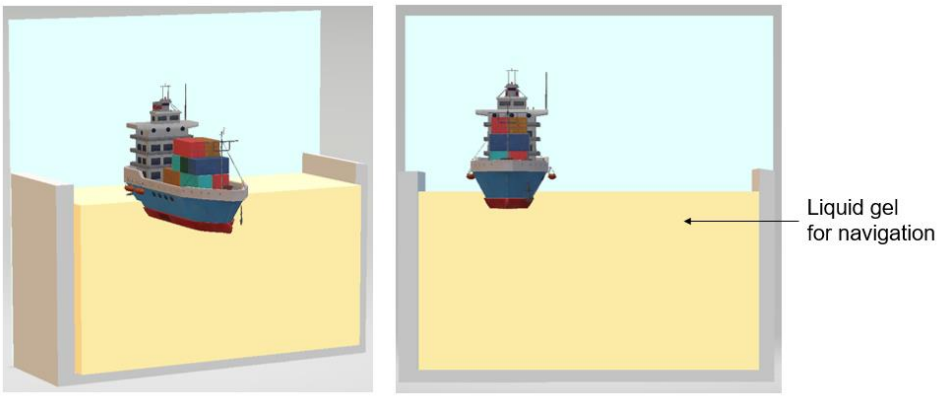


Figure B4: Liquid gel in small channel

B5. Concept 5: Liquid gel in the access channel

In the opening of port of Rotterdam an access track is designed in the bottom of the sea with a constant depth of 21m to allow incoming ships to enter safely the port area. The shape of the track where the gel is placed is not constant, as the channel is shallow in the open sea waters and needs to get deeper close to the port. However, for this estimation the dimensions were kept constant and are (L, W1, W2,H)=(5km, 120m, 60m, 1m)

The total volume of product in the track is estimated to be ≈0.45M m^3 with the material cost reaching 5M€. The expected reduction in dredging volume is assumed to be 80% to perform the relevant cost estimations. The actual reduction that can be achieved needs to be estimated with a computation model based on the hydrodynamic conditions in the area.

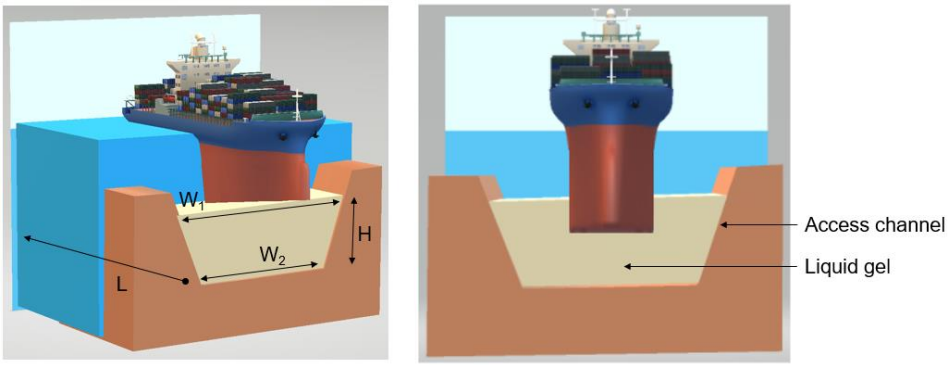


Figure B5: Liquid gel in access channel

B6. Concept 6: Gelation into sedimentation traps

The final concept describes the use of gelation agents in sedimentation traps to ensure better sediment retention. As it can be seen in Figure B6, the sediment can be removed from the trap from water currents. The addition of the gel will promote flocculation in the trap, allowing for collection of bigger quantity of sediment in the trap. The dimensions of the trap can be found also in Figure B6. It is assumed that double mass of sediment can be collected in the trap and therefore less dredging will be needed. The reduction of dredging frequency that can be achieved is not known yet. Therefore, an estimation has been made to complete the specifications list and get a first idea of the order of magnitude of cost that can be saved. The estimated reduction with this method is assumed to be 80% in comparison to a sedimentation trap without the added gelation agent. This assumption needs to be confirmed experimentally once the final gelation agent is identified.

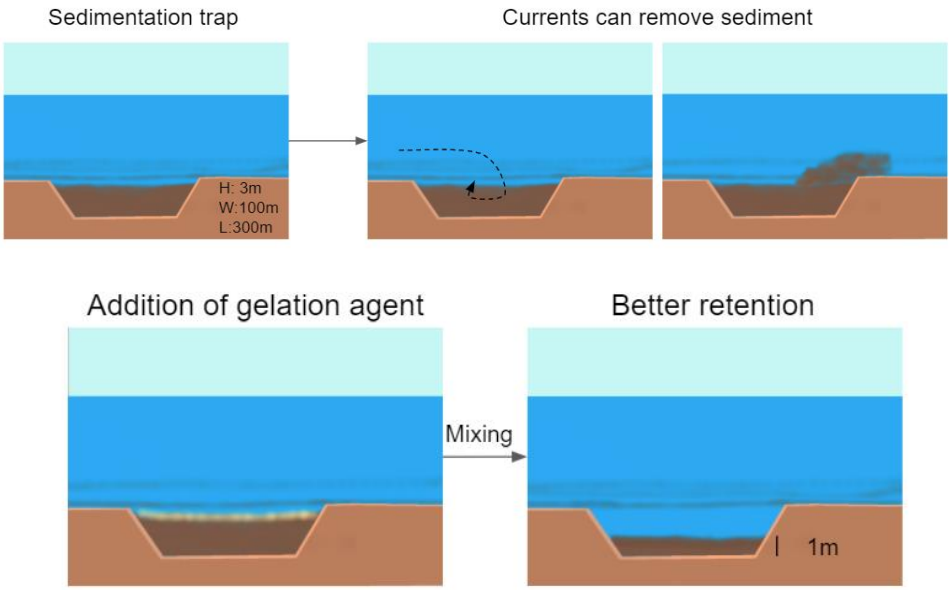


Figure B6: (Above) poor containment of sediment in sedimentation trap; (Below) improved sedimentation and retention with the use of a gelation agent.

Appendix C: Lab Samples

In this paragraph it is explained what gel samples have been made in the lab with respect to their ingredients and concentration. The samples that were made in this project consist of a gelation agent, a dispersion medium and in some cases other added solids to increase the density of the final gel (mud or clays). Initially, the gum was added slowly and in small portions in water under constant mixing with a cooking mixer. The samples were considered homogenized once lumps (fish-eyes) were no longer observed visually. The addition of the mud suspension was added in the last step of sample preparation.

C1. Sample Codes

The samples that were made were given a code as a name so they can be easily identified. The letters indicate the gelation agent and added solids whereas the number next to them show the % w/w concentration of the ingredient as dry equivalents. Table C1 shows the abbreviations used for naming the gel samples, their meaning and the origin of the raw material.

Table C1: Explanation of codes in samples made

Code	Description	Supplier/ Origin
XG	Xanthan gum	xanthomonas campestris, 43708, lot#BCBV5654, Sigma
GG	Guar gum	G4129, Lot#SLBZ5048, Sigma
CMC	Carboxy Methyl Cellulose	Medium viscosity, 21902, lot#BCBVN1690V, Sigma
NaCl	Sodium chloride	Diluted from sea water recipe, deltares
Mud	Mud	from sedimentation trap in Botlek
Kau	Kaumera suspension	7% w/w from Friesland Campina process, (batch 3/21)
Clay	Pottery clay	K122, Sibelco, Fuchs keramische massen
I	Ilite	Argile verte, Lot: 258.20arqiletz
S	Small particle size	around 6µm
L	Large particle size	> 400 µm

It was assumed that the polymers used were dried 100%. Loss on drying (LOD) was performed for the Mud and Kaumera suspension as well as for the Ilite before the samples were made. The LOD was done on a small sample of the suspension at 105°C for 12h or until constant weight. The summay of LOD in the ingredients used is presented in Table C2, and Table C3 shows the codes from the gels that are presented in this report.

The two batches of Kaumera that are available in the lab come from different sites and are produced with different type of feed. The older batch uses as feed water waste from the Nereda treatment, whereas the newer batch uses incoming feed from Friesland Campina and shows different behavior with respect to the time of achieving flocculation. In the experimental trials only the second batch from Friesland campina was used. Specially 2 different manufacturing batches were available, from March and July 2021 with solid content of it was 7.5% and 8.3% w/w respectively.

Table C2: Loss on drying and solid content for the materials used

Material	LOD %	Solids content, % w/w
Consolidated mud	68.5	31.5
Mud suspension	72.6	27.4
Kaumera suspension	92.5	7.5-8.3
Ilite	4.7	95.3
Clay pre-hydrated	39.2	60.8

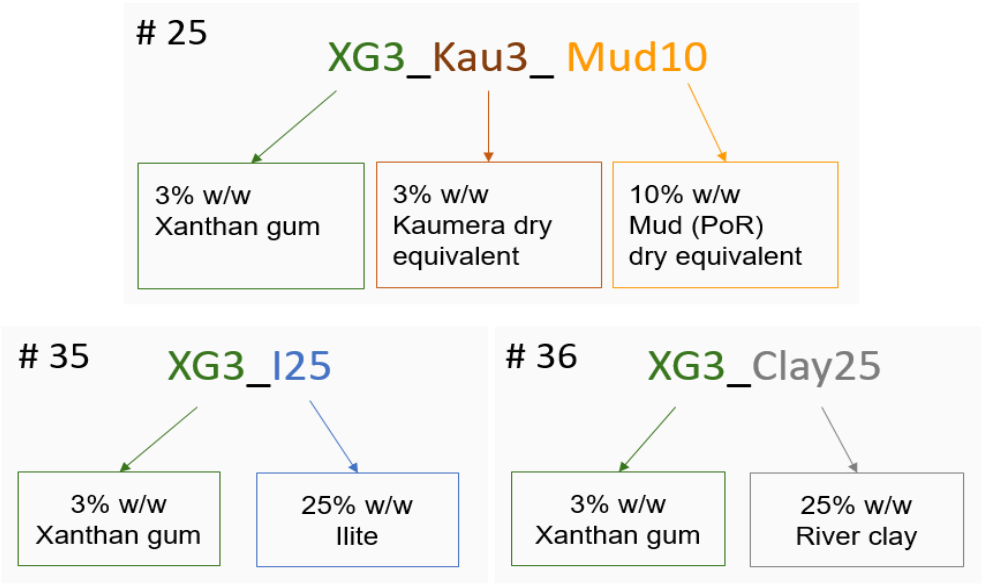


Figure C1: Explanation of code naming

Table C3: Name and codes of samples made in preliminary trials

#	Code	#	Code	#	Code	#	Code	#	Code
1	XG1	**11**	GG5	**21**	XG3Kau0.7Mud14	**31**	XG3Kau0.7I10_S	**41**	XG1Mud25
2	XG1	**12**	XGGG3	**22**	Kau3Mud11	**32**	XG3Kau0.7I10_L	**42**	CMC5
3	XG3	**13**	XGGG1	**23**	XG3Kau0.7I50	**33**	XG3Mud25	**43**	CMC5Mud5
4	XG5	**14**	XGGG1I5	**24**	XG3Kau4.5Mud5.5	**34**	XG3I25	**44**	CMC5Mud10
5	XG1I5	**15**	XG1Nacl1	**25**	XG3Kau3Mud10	**35**	CMC3	**45**	CMC5Mud20
6	XG1I5	**16**	XG1I5NaCl1	**26**	XG3Kau1.5Mud16	**36**	XG3Clay25	**46**	CMC5Mud25
7	XG1I10	**17**	XG3Mud24	**27**	XG3Mud20	**37**	CMC10		
8	XG5I5	**18**	XG3Kau0.7I10	**28**	XG3Mud10	**38**	CMC10Mud25		
9	GG1	**19**	Kau3I40	**29**	XG3Kau5.5	**39**	XG1Mud10		
10	GG3	**20**	Kau0.7Mud14	**30**	XG3Kau3	**40**	XG1Mud20		

C2. Additional Rheological data

The gel samples that were manufactured in the lab were rheologically characterized with the use of the HAAKE™ MARS™ rheometer. The types of measurements that were performed are:

- Controlled shear rate (flow steps) measurements,
- oscillatory measurements, like frequency sweep and temperature ramp.

The geometry that has been chosen for these measurements is a parallel plate type with serrated surface as it can keep stiff samples in place avoiding wall slip during the measurement. A bob and cup type of geometry is typically used for suspensions with lower viscosity.

Flow step measurements

The relationship between shear stress and shear rate was recorded for all samples 1-7 days after the sample preparation. For each sample the measurements were repeated at least twice to ensure that the results are relatively consistent. The graph in Figure C2, show the observed relationship between shear stress and shear rate for a sample containing XG, Kaumera and Mud.

From the graph it can be concluded that the sample exhibit non-Newtonian behavior and the shear stress reaches a plateau at shear rates above 1 s^{-1}. The material is also shear thinning as its viscosity is reduced with increasing shear rate.

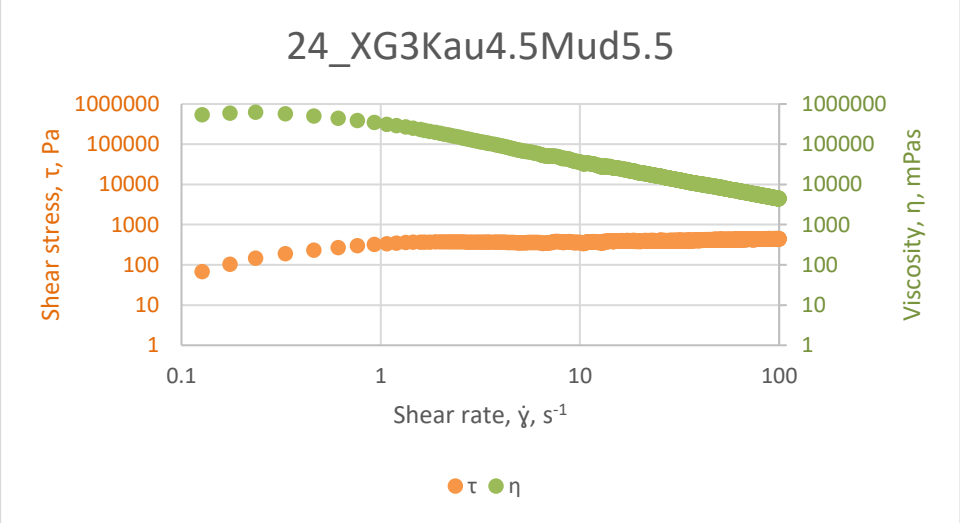


Figure C2: Flow step measurement of a gel sample

Oscillatory measurements

For selected samples additional oscillatory measurements were performed to investigate the gel behavior further. In this paragraph two examples of samples tests will be presented, a frequency sweep and a temperature ramp. The frequency sweep is a type of measurement that provides information about the viscoelastic properties of the sample at different frequencies. The value of the elastic (G') and viscous (G'') modulus as well as the difference between them can provide additional indication about the microstructure of the gel network. Figure C3 shows the measurement of the viscoelastic properties for a stiff gel sample that contains XG, Kaumera and mud.

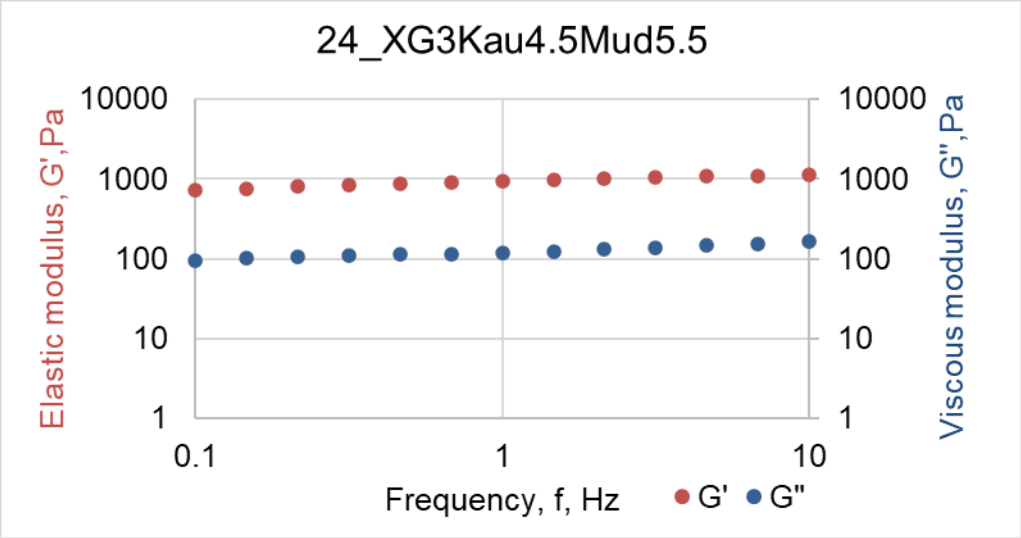


Figure C3: Frequency sweep for gel with 3% XG, 4.5% Kaumera and 5.5% w/w mud

The G' and G'' remain stable with frequencies up to 10 Hz and no crossover point is observed. Thus, the presence of a stable gel network can be confirmed. Additionally, the difference between the viscous and elastic moduli with the combination of the highly measured values (1,000Pa/ 30Pa) indicates the presence of a strong network.

Finally, for a few samples, a temperature ramp was performed from 5 to 20^{o}C to study whether the gel properties change at colder environment. This specific range was selected as it is the difference of sea temperature throughout the year. The result of a gel sample containing XG and mud is presented in Figure C4.

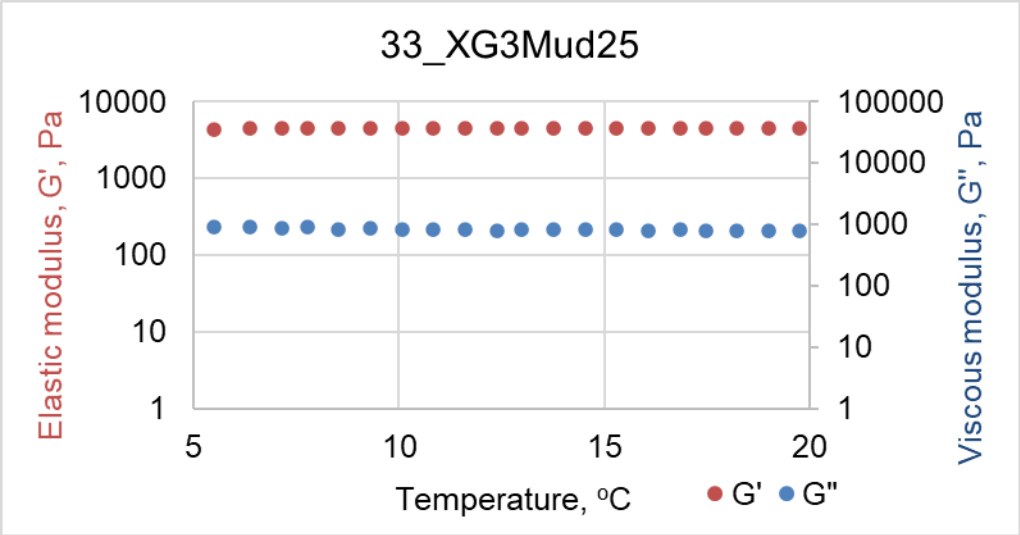


Figure C4: Temperature ramp of a sample containing 3% XG and 25% w/w mud

The above graph shows that the gel properties are independent on the temperature in the desired range. Therefore, the gel is expected to exhibit the same rheological characteristics within the range of 5-20 °C. The difference in the two measured properties is also significant (5,000Pa/ 200Pa) and thus the gel also has a strong gel network. Comparing the two graphs in Figure C3 and C4, the absolute values in sample 33 are higher and therefore the gel will be stiffer than # 24.

Comparison between Mud, river clay and Ilite

Three samples were made and compared rheologically to assess how various clays alter the yield stress of the gels:

- 3% w/w XG and 25% w/w mud
- 3% w/w XG and 25% w/w river clay
- 3% w/w XG and 25% w/w Ilite

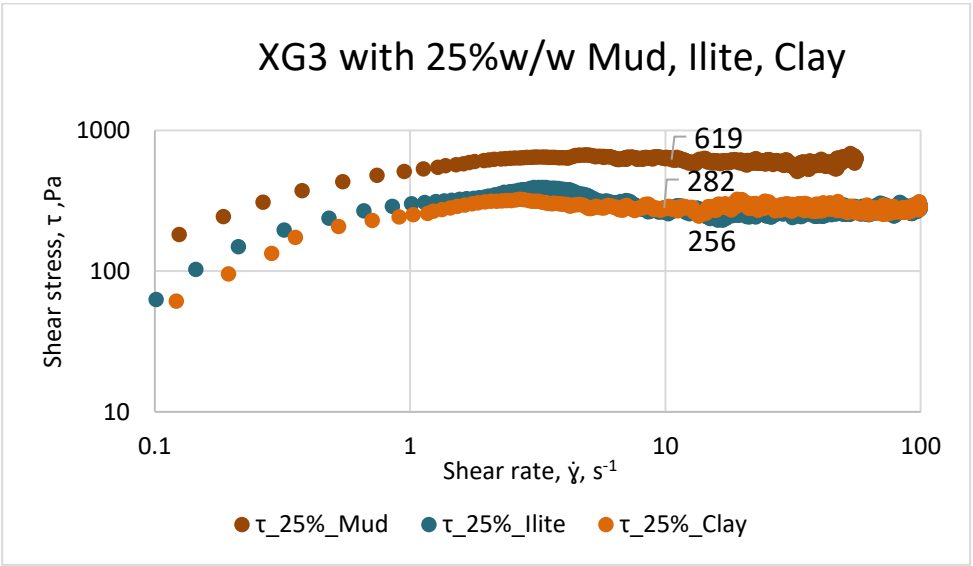


Figure C5: Shear stress curves for gels with 3% XG and 25% dry Mud, Ilite, or clay

Effect of particle size on gel strength

During the preliminary study the effect of particle size in the gel strength was also studied with the use of Ilite powder. The sample preparation can be viewed in detail in Appendix D1. The result is presented in Figure C6 below.

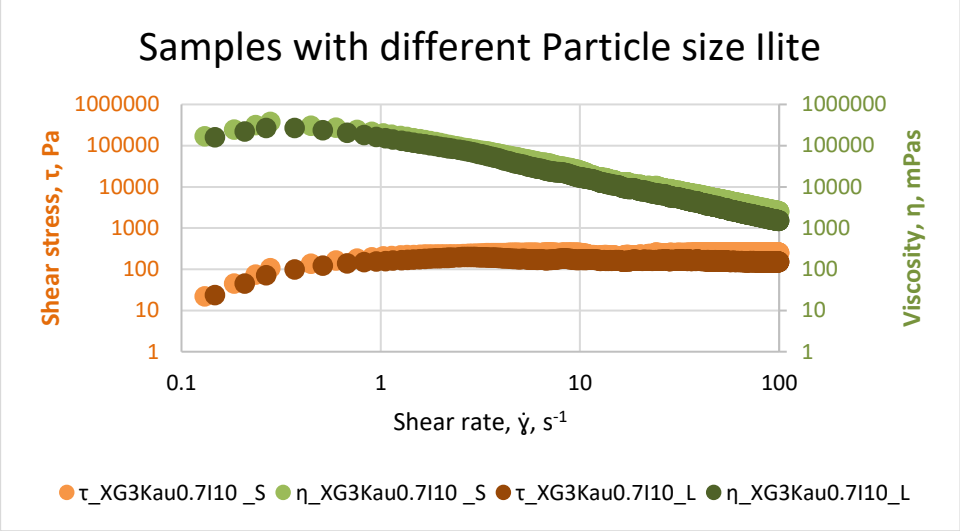


Figure C6: Comparison of samples with Ilite of different particle size

The results suggested that when smaller particles of solids are used the shear stress that can be achieved is higher. The dark orange curve refers to the sample containing Ilite particles of large size (> 400 µm), whereas the light orange gel contains Ilite that was previously dispersed in water and thus has a smaller particle size (< 60 µm). The measured shear stress for the smaller particle size is higher for all the recorded shear rate values.

Effect of 1% w/w salt

Two samples were additionally prepared to if the salt concentration of 1%w/w will affect the strength of the gels. The concentration was chosen since it is the average content of salt that is found in Botlek area. One sample with 1% xanthan gum and 5% Ilite was prepared and compared with the same sample when 1%w/w is added. The salt was added by diluting the sea water recipe (available in Deltares) at the desired concentration. This medium was used for the 2nd sample preparation instead of water (Comparison in Figure C7).

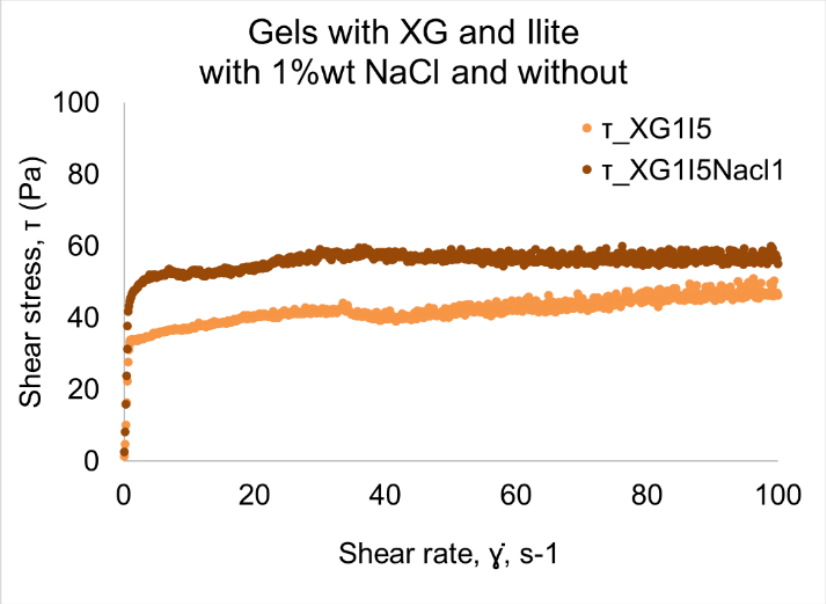


Figure C7: Effect of 1% w/w salt in gel formulations

The gel sample that contains salt has a higher shear stress than the sample without it. Therefore, salt can affect the final strength of the created gel. Once the gel recipe is defined an additional sample with added salt will be made to check how much the final sample is affected. Higher concentration of salt can be considered for these experiments up to 3% w/w.

Comparison xanthan gum – guar gum and mixtures

A series of samples were made containing XG, GG and mixtures of the two agents. The combination of these two ingredients in a ratio of 1:1 has been reported in the literature to result in a stronger gel with higher viscosity when compared to gels with the same concentration of one ingredient (Casas et al., 2000). A comparison of the samples made in the lab is available in Figure C8.

From the graph in Figure 6.8, it can be concluded that the mixture of 3% w/w of both XG and GG (1.5% each) will have at least as high rheological properties as one of the ingredients or slightly higher (red line in the graph). More testing is needed to form clear conclusions however it seems possible that a combination of the two ingredients has the tendency to create stronger networks

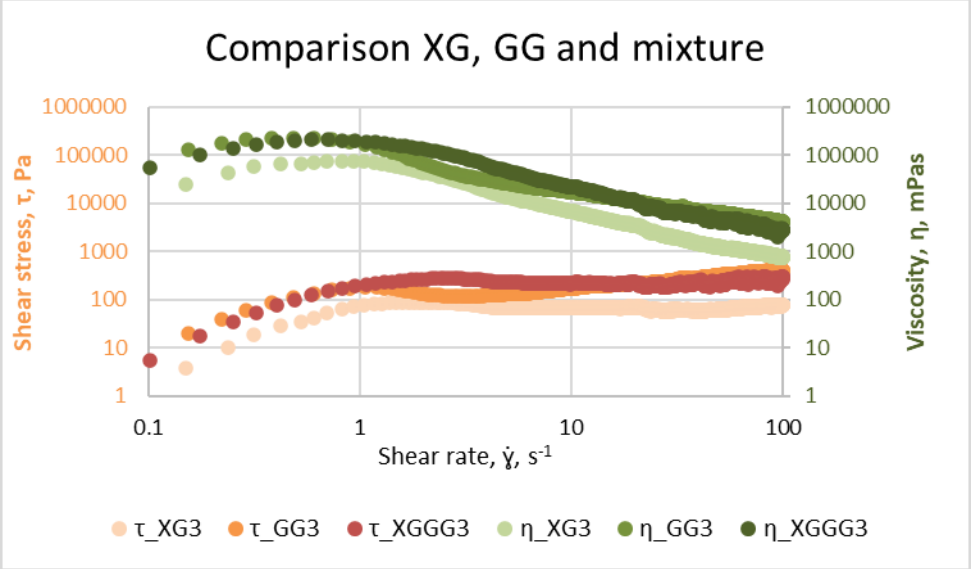


Figure C8: Viscosity and shear stress of gums and mixtures.

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C3. Preliminary Stability of stiff gel barriers

Stability in tap water overtime

The stability of the stiff gels was evaluated with underwater experiments. A small portion of the gel was placed into a transparent beaker and tap water was slowly added on the side of the wall of the beaker. Around 10 g of sample were used in each trial and 300ml water. The tests were performed at room temperature (at 21°C) over a period of 5 weeks. An example of an underwater study over 3 days can be seen in Figure C9 (see Section C1 for gel names).

The underwater trial suggested that swelling occurs on the gels once they placed in water. The degree of swelling was not investigated in these trials, however, the photos suggest that shape deformation is to be expected when the gel product will be placed in the port. Gels that contain Ilite tend to disperse faster when little or no gelation ingredient is used. Gels that contain high content of polymers (XG or Kaumera) and do not have a big concentration of added solid particles (like mud) have a lower density and the float instead of remaining submerged.

Therefore, the ratio of gelation compounds and solids need to be carefully tuned to achieve the desired product density. The density of the water at the end of the trial does not change significantly. Based on reverse trials, it was also proven that gel might stick on the glass surface under dry conditions. However, submerging the barriers into water does not show this effect. Sand has also been used in many trials to increase the roughness.

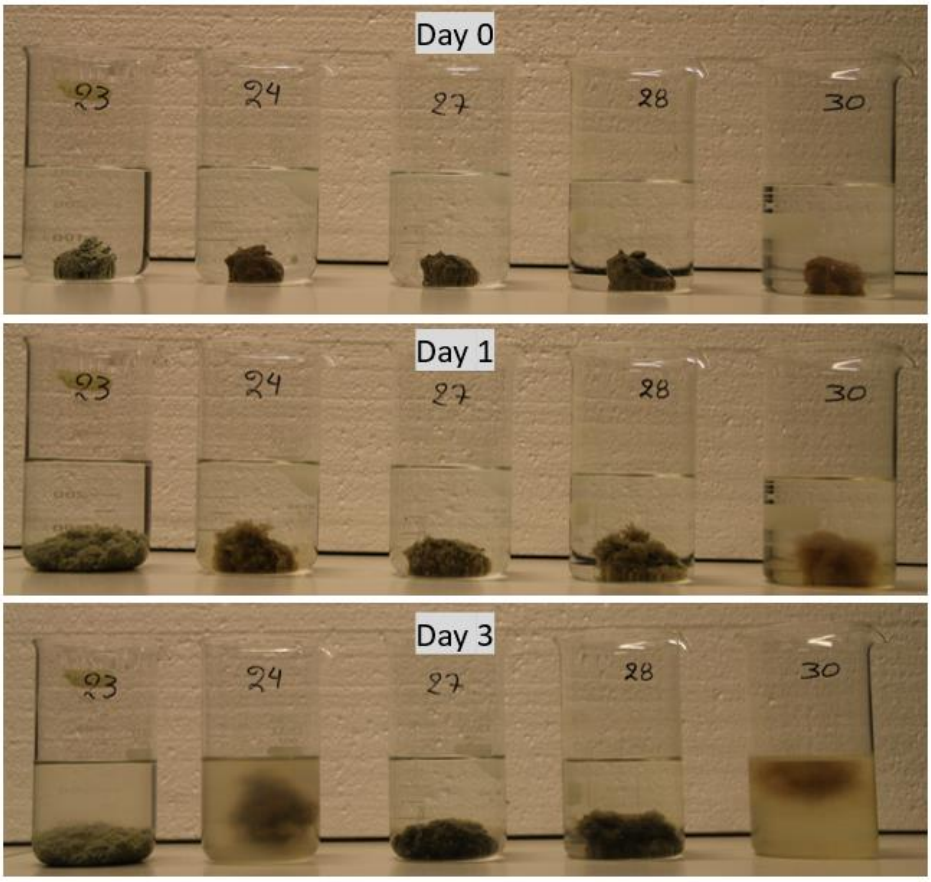


Figure C9: Underwater 3-day stability test for various samples

Gels with Kaumera

Some of the gels that were manufactured in the lab were containing Kaumera at concentrations up to 3% w/w. Trials that also contain xanthan gum, mud suspension or Ilite have been made. The main results are presented in the following paragraph.

Samples made with Kaumera and mud resulted in liquid gels, with low strength. The data are provided in figure C10 and C11.

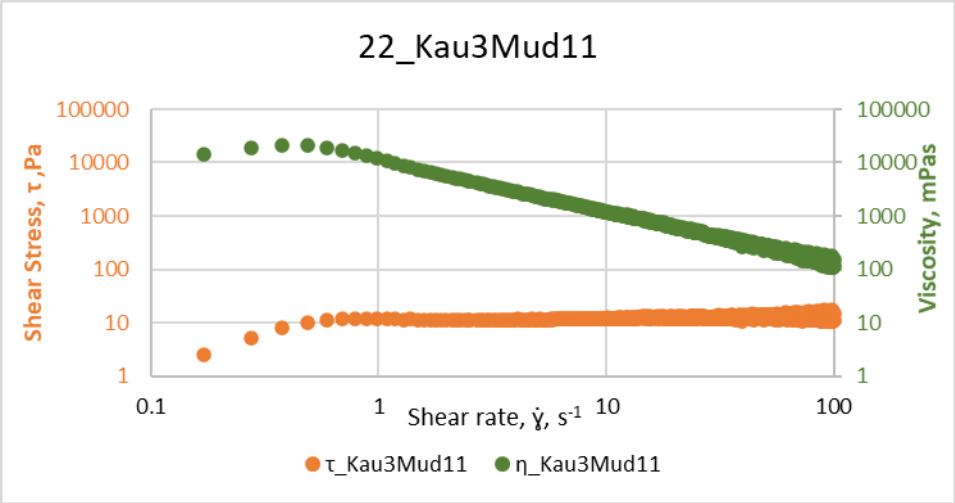


Figure C10: Liquid like sample with 3% Kaumera and 11%Mud

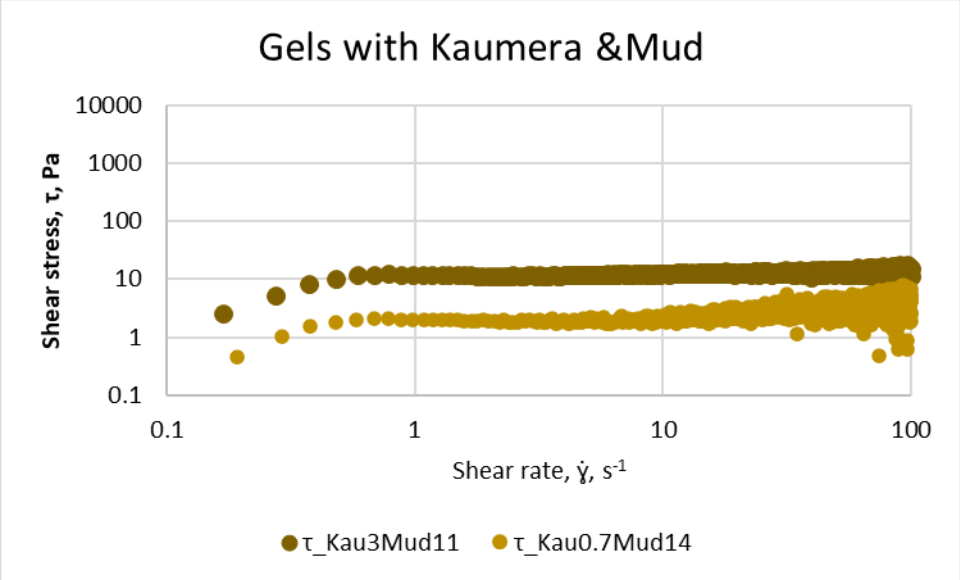


Figure C11: Comparison of samples with Kaumera and Mud

Kaumera gels made with xanthan gum and water alone are not dense enough to remain underwater. Air is incorporated into the gel structure during sample preparation. As it is shown in Figure C12 swelling of the gel lowers the overall density of the gel which leads to flotation. On the contrary, gels that contain higher solids content, (Figure C13) have higher mass and their density remain high enough even after swelling occurs, thus they remain submerged underwater.

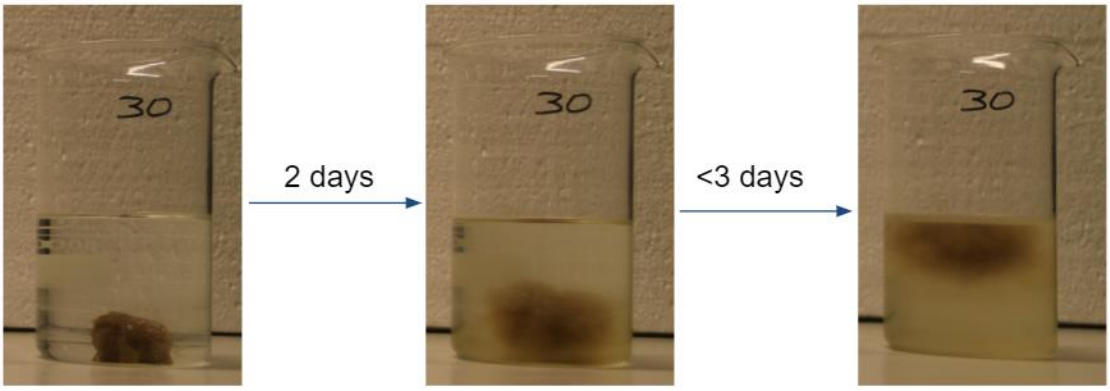


Figure C12: Underwater stability of a gel sample containing 3% Kaumera and 3%w/w XG

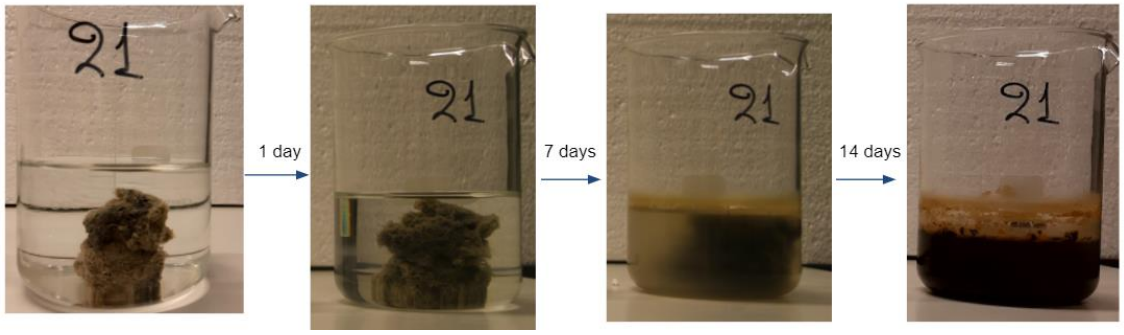


Figure C13: Gel sample with 3% XG, 0.7% Kaumera and 14% w/w mud

Attempts to create stiff samples with Kaumera and mud in the absence of a gelation agent were not successful as the Kaumera sample is very diluted for this application. At this moment the provided Kaumera suspension is not concentrated enough to provide sufficient degree of gelation in the final product and for this reason high concentration need to be used to create stiff gels.

The use of Kaumera as a flocculant is another possible application that might be more feasible.

Appendix D: Details of Unloading technique

D1: Delivering the mixture through a pipe

The first application method utilizing existing pumping equipment available in PoR/RWS area in the port to place the mixture through a pipe on the desired location. A hopper dredger as shown in Figure C1 could be used for this procedure, as existing dredging equipment is used for beach nourishment. The accuracy that can be achieved with this technique is relatively high, as the product is applied closer to the channel and floor and is thus less likely to be carried away by currents. As an assumption the gel can be applied within 1m radius from the desired location. A requirement for this method is that the material applied has a shear thinning behavior, thus it will flow after applying a shear starting stress.

D2: Fascine mattress to let the material sink on location

A second technique is the use of a fascine mattress (a.k.a Zinkstuk) as a supporting structure that sinks slowly over time to the bottom of the channel.



Traditionally, once the mattress is brought above the desired location rocks are being deposited on it in a control way on location. The technique has been used to protect riverbanks from erosion. The material is made usually from bundles of brushwood and can be formulated in any size. An example of a zinkstuk is shown in Figure D1.

Figure D1: Fascine mattress for use in port (Van Aalsburg, 2022)

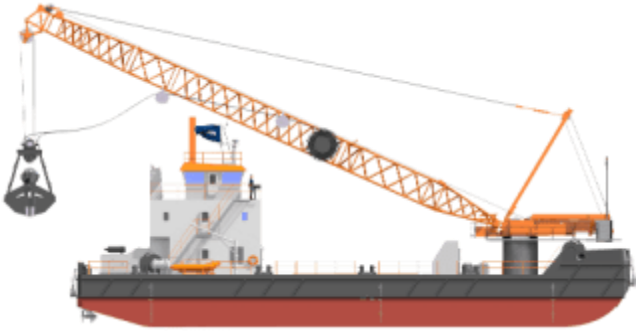
The gel product can be placed on top of this slowly sinking plane and then remain in the desired location. The material that the fascine mat is made from is, however, not navigable by vessels and thus must be removed after the placement of the desired product.

Another solution would be to pretreat the channel floor by increasing the depth (around half meter) to compensate for the heigh of the Zinkstuk. This way, the mattress will remain below the depth for navigation. Removing the mat after placement of the gel product could also be considered but is more complicated to achieve and training of the personnel might be required. In the case of mat removal, the barrier will need to be pushed away after sinking, thus the accuracy of placement is estimated to be less than 10m from target. Finally, it can be considered to design a new type of biodegradable fascine mattress that can dissolve naturally in water a few hours after application.

The cost estimation of manufacturing a fascine mattress was based on data provided for brush mattresses made for stability of ground on slopes (12-24$/m^2) (Allen & Fischenich, 2001). An assumption was made that the cost involved for making a fascine mat will be 20 €/m^2.

D3: Placing the gel with a grab barge vessel

Vessels with an incorporated grab equipment can also be used to place material in the desired location. Those crane barge vessels are commonly used in port operations. The capacity of each loading can reach up to 400t (Damen, 2022). A quick representation of a crane barge vessel is shown in Figure D2.



Similarly, grab equipment placed on land could be used when the gel product is easily reachable from the terminal. The time required to deliver bigger volumes of gels is limited to the number of (un)/loadings that can be achieved within working operating hours.

The advantage of this method is that operation cost is the same for every gel stiffness.

Figure D2: Crane barge vessel (Damen, 2022)

D4: Using a split barge to discharge the product

The last method discussed is the use of a barge split hopper vessel to rapidly dispose large quantity of the gel product on site (Figure D3).

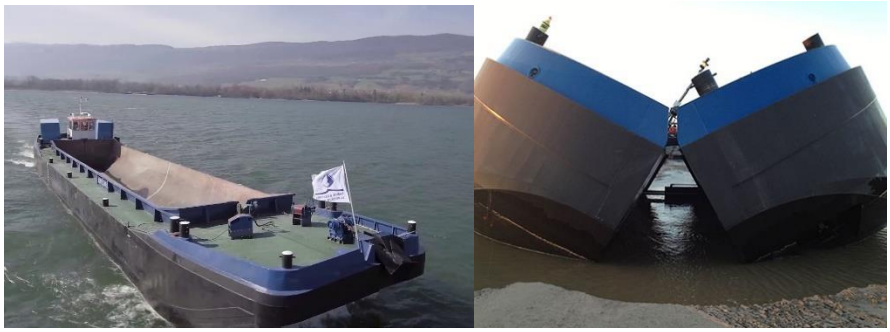


Figure D3: Barge split hopper while navigation (left), at use (right)

This vessel can split open its structure and release the material above the desired location. The accuracy of placement is lower than the previous described methods, especially in areas with strong currents. It is estimated that placing the gel can fall possibly up to 100m away from the target. The capacity of these type of vessels can reach up to 2300 m^3 (Baars Sliedrecht, 2021) (Boskalis, 2012).

Appendix E: Mixing and unloading strategy for concept structures

Analyzing the six structure concept ideas has not been performed yet in a detailed manner, as it is not clear which structure will be feasible in large scale and will contribute the most to the reduction of dredging costs. However, a quick evaluation has been made in a matrix to assist in future development of an application strategy. This table can serve as a guide that highlights the most appropriate technique for the various gel concepts (barrier to liquid gels). In Table E1 the various concept structures are evaluated quantitively or qualitatively against the three main mixing methods and four unloading procedures that were discussed in Appendix D. Table E2 summarized the characteristics for each unloading method.

Table E2: Characteristics of unloading methods per concept.

Method	Equipment	Capacity (m^3/h)	Power (kW)	Literature
Pumps	Dompel pump	45-2,000	5.5-315	(MST, 2022)
	Bredel type	Up to 108	NA	(Watson-Marlow, 2022)
	Ecodelta pump	Up to 20,000	1,500	Personal communication Andre Hassent, 15/02/22
In-line mixers	Silverson 150/250	750-6,200 (kg/h)	NA	(Espinoza et al., 2018)
	ALVAK mixer	90,000 (kg/h)	0.55-55	(Vak Kimsa S.A, 2022)

With respect to the pressure that the pump head can generate, the submersible type of pumps are less strong than the bredel type (up to 19 bar). However, with the current experience in port of Rotterdam pumping from 20 meters depth is possible with a series of dompel pumps as they can be submerged and operate at various depths.

Detailed cost estimation was not performed at this project phase, thus additional costs for renting dredgers, barge and pontoons is not included in the estimation. The cost estimations, presented in the previous paragraphs were made based on the power consumption of the equipment in use and the operation hours necessary to handle the desired volume of gel product. The cost of electricity was assumed to be equal to the electricity cost for industry provided by *statista* in February 2022 (Alves, 2022). A more detailed analysis should also be performed when the exact manufacturing steps and the location of the barrier is confirmed.

For the operation of the grab equipment the cost per volume was extracted form a report related to the freight transport of goods in port of Rotterdam. The unit of 1.12€/m^3 refer to the operational cost of heavy trucks (LZV) while moving bulk material via road transport (Van der Meulen et al., 2020). The capacity of the grab barge vessels was estimated based on the details found in contractor sites, collaborating with PoR, ranging from 45-400 ton (Damen, 2022). For the calculations it was assumed that 4 x 500 m^3 of gel product can be handle with the grab within one hour, thus 15 minutes loading between each grab cycle of loading and unloading.

The cost of operation for dry and liquid bulk cargo on large ships is 0.028 and 0.030 €/ton/h respectively (Van der Meulen et al., 2020). Finally for the dimensions of the fascine mattress the footprint of the gel barrier was estimated to be 4,000 m^2 (100 m x 40 m).

Table E1: Comparison guide for mixing and unloading concept selection per concept structure.

			1.Gel barrier	2.Drydocks	3. Gel slope	4. Access channel	5.Liquid in channels	6. Gel in traps
Mixing method	Mixing Cost €/product	Pre-mixed	260	1,600	1,150	21,500	71,000	1,150
		Mixed in Barge	60	360	262	5,000	16,500	262
		Mixed In-line	370	2,500	1,600	30,500	110,000	1,600
	Mixing time h/product	Pre-mixed	1	6	4	82	273	<1
		Mixed in Barge	1	6	4	82	273	<1
		Mixed In-line	1	6	4	82	273	<1
Unloading Method	Placing cost €/product	Via Pipe	low; 220	low enough; 1,300	low; 950	high; 18,000	high; 60,000	low; 32
		with grab	low enough	high	high	too high	too high	low enough
		with split barge	low enough	high	high	too high	too high	low enough
		zinkstuk	low	low	low	NA	NA	NA
	Placing time h/product	Via Pipe	fast; 1h	less fast; 6h	fast; 4h	slow - 4days	very slow - 12days	very fast <1h
		with grab	fast; <3h	slow; 17h	slow; 12h	too slow; 1week	too slow; 1month	fast <30min
		with split barge	fast; <1h	less fast <5h	fast <4h	not so fast <3 days	slow >1 week	very fast <30min
		zinkstuk	fast enough; >2h	less fast >4h	less fast; 4h	NA	NA	NA
	Placing accuracy	Via Pipe (<1m)	High enough	High enough	High enough	higher than needed	higher than needed	High enough
		with grab (<2m)	High enough	High enough	High enough	higher than needed	higher than needed	higher than needed
		with split barge (>10m)	too low	too low	too low	sufficient	NA	sufficient
		zinkstuk (<10m)	High but complex	High but complex	too low	NA	NA	NA

Appendix F: Possible placement locations in RWS

In this paragraph additional locations for gel products are presented in the RWS area after an email communication with Lievens, R. 27th October 2021. These locations are indicated with red lines in the Figure F1 below.

The gel barriers that could be applied in the above-mentioned locations refer to underwater deflection barrier that will remain below navigable depth. The properties of the barrier, with respect to strength and stability should be further adjusted according to the local hydrodynamic conditions. In these locations the gel product can potential help lower the spread of sediment or control low density salt currents that originate from the sea.

A detailed analysis of the above idea is not explored in detail as the current gel barrier cannot withstand the high-speed currents on those locations. However, it is worth mentioning these areas as a starting point for future research for other potential products.



Figure F1: Potential gel barrier locations in the waterway of RWS

Appendix G: Details of application ideas

The common characteristics of the three methods refer to:

- Preparation and application of **a 5,500 m^3 gel barrier** with XG and dredged mud
- With thixotropic behavior and a yield stress of around **250Pa**
- In a timeframe of around **4 hours**
- Applied in **Botlek** area in the port of Rotterdam (distance **2km** from terminal)
- Concentrated 3% wt XG solution can be prepared in a **nearby site** (**5Km** from terminal)
- **Without** accounting the **curing time** for the gel product
- With approximately **15 minutes** placement time underwater **via a pipe**
- With the same amount of dredged mud
- With the assumption that the desired gel **quality** can be **achieved** with each method
- **Excluding** the **capital** investment cost of mixers

G1. Batch preparation of gel barrier in barge

The first design idea is to create a premade solution of xanthan gum with dredged mud close to the terminal, homogenizing the mixture on a barge vessel by circulating the mixture with the help of dompel pumps. Another pump that could also be considered is the Bredel-hose type, which is a patented product that can handle complex mixtures of solids and liquids on site. However, since many specifications of this pump were not available online, for simplicity the concept idea and the calculations on the upcoming paragraphs were made with a dompel pump. A schematic representation of this application concept is shown in Figure G1.

To ensure sufficient homogenization of the final mixture, XG needs to be applied as a premade concentrated solution made with an industrial mixer on a different site. The amount of XG required is around 2,100 m^3 as a 3% w/w solution which can be transferred to the terminal with land transport. It is assumed that the preparation of XG can take place on a nearby-site, located around 5 km from the terminal. After formation of the barrier mixture the barge vessel needs to travel back to the desired location (2km) to dispose the gel via a pipeline.

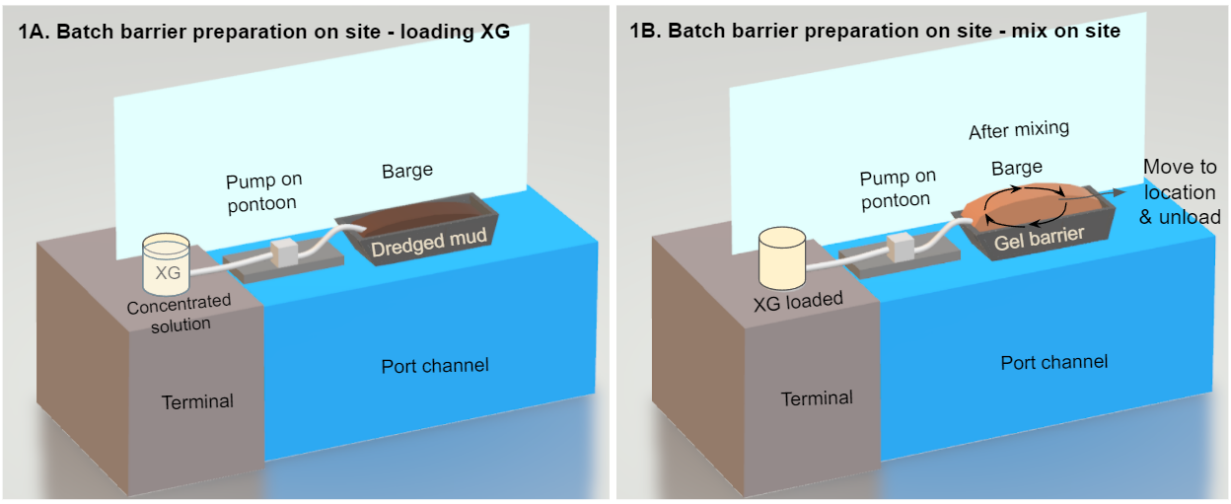


Figure G1: Batch preparation of the gel barrier on a barge vessel;
(Left): loading of XG on dredged mud, (Right): formation of a gel barrier after mixing

G2. In-line mixing & continuous formation on site

The second concept proposes the use of in-line mixers to manufacture the gel barrier directly on the desired location. In Figure G2 it is graphically shown what procedure needs to be followed. Dry xanthan gum (around 50kg) is transferred in bags in via the waterway (2km) on the application site. The powder is slowly added on the inline mixer while pumping the dredged mud into a barge vessel. In this case 3 in-line mixers need to be utilized to process the overall volume of the gel barrier within one hour. With this method the transportation cost of the xanthan gum solution and dredged mud is eliminated.

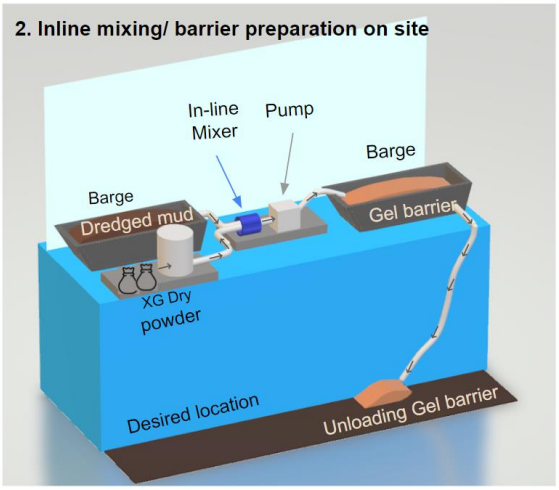


Figure G2: Continuous in-line preparation of the gel barrier on the desired location

G3: Application of premade gel barrier

The final concept idea suggests that the gel barrier will be made in an industrial site close to the terminal (<5km). The dredged mud will be transferred to the site via water and land, and then mixed with a 3% w/w XG solution with the use of industrial size mixers. To manufacture around 5,500 m^3 a series of mixers will be required. The final volume of the barrier will need to be transferred back to the desired location. This concept results in higher preparation costs but will simplify the procedure that the operators need to follow on the port location.

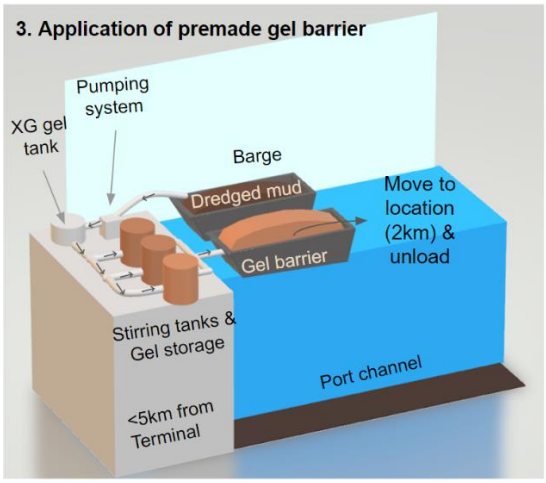


Figure G3: Application of premade gel barrier from industrial site to port channel