



FACULTY OF SCIENCE AND TECHNOLOGY

MASTER THESIS

Study program / specialization:
Environmental Technology / Offshore
Environmental Technology

The spring semester, 2022

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Thesis title: Destabilization of crude oil sludges by chemical and mechanical treatment

Credits (ECTS): 30

Keywords:
Crude oil sludge
Destabilization
Emulsion
Hazardous waste
Waste treatment

Pages: 84

+ appendix: 24

Stavanger, 15.06.2022
date/year

Acknowledgement

This thesis is submitted as a final fulfilment of the requirements for the Master's degree in Environmental Technology at the University of Stavanger.

I would like to express my deepest appreciation to my external supervisor from Norwegian Technology AS, Stig Ovar Keller, for the great support, enthusiasm, knowledge, and for being a great companion during this work. I dedicate special gratitude to Evgenia Hernandez for the great support, constructive feedback, knowledge, and guidance.

I would like to give my sincere gratitude to my internal supervisor Skule Strand, for the guidance, good discussions, and feedback.

Abstract

The demand for petroleum is still increasing. As a result, various wastes are generated during exploration and production, even though strict rules and regulations are applied to oil and gas industries to optimize waste management programs. The refineries still produce significant amounts of crude oil sludges formed at the bottom of crude oil storage tanks. This waste is identified as hazardous waste. The accumulation of crude oil sludges negatively impacts the storage capacity and the safe operation of the storage tanks.

This study presents the problem connected with crude oil sludges and the alternatives for its treatment. In favor of minimizing the environmental impact caused by oil sludges, the primary strategy for its treatment is to separate the sludge into its main components: oil, water, and solids. The oil in the sludge may be considered a recovery source. The sludge's complex composition and properties were comprehensively described on how to separate the sludge. A method for destabilizing and separating the sludge into three phases was proposed and tested on two types of sludges (Mongstad sludge and Brenda sludge).

Chemical destabilization of crude oil sludges by adding different MudSplit chemicals followed by centrifugation proved to give a positive result. The results showed how variables in sludge composition and properties challenge the treatment process of this waste. Temperature and pH were enhancing factors for Mongstad sludge's destabilization. Heat energy reduced the viscosity of the sludge, and the addition of MudSplit chemicals also reduced the viscosity. Mongstad sludge gave three-phase separation, where in most samples, the upper phase contained >90 % oil and was free of water. The effect of the tested MudSplit chemicals was not comprehensively observed under the different experimental conditions. Brenda sludge showed to be more difficult to destabilize. It was possible to separate the sludge into three distinct phases through chemical and mechanical treatment. The best results for Brenda sludge were recorded using MudSplit6.

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List of abbreviations

E&P	Exploration and production
FW	Formation water
NAs	Naphthenic acids
O&G	Oil and gas
OWR	Oil/water ratio
PHC	Petroleum hydrocarbon
PAH	Polycyclic aromatic hydrocarbon
RCF	Relative centrifugal force
TPH	Total petroleum hydrocarbon
O/W	oil-in-water
O/W/O	oil-in-water-in-oil
W/O	water-in-oil
W/O/W	water-in-oil-in-water

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1. Introduction

The petroleum industry generates huge amounts of waste. As the exploration and production (E&P) of crude oil is still increasing, its generated waste is receiving greater attention. Consequently, waste management and sustainable technologies have become an important industry aspect. Proper waste management planning is key to achieving sustainable and environmental waste management. Lately, crude oil sludges have received greater attention due to its hazardous nature, difficulties in treating and its huge accumulation worldwide.

1.1 Project description

Both the upstream and downstream operations in the petroleum industry generate huge amounts of crude oil sludges. Oil sludge is identified as hazardous waste solids in many countries (Hui et al., 2020) and listed as hazardous waste in Resources Conservation and Recovery Act (USEPA, 2012). The main idea of this thesis is to present the problem connected with crude oil sludges and the alternatives for its treatment.

Due to the increased production of oil sludge, proper waste management has received greater attention (Johnson & Affam, 2019). Improper disposal or insufficient treatment of oil sludge can cause severe threats to the environment and human health (Jerez et al., 2021). To minimize the pollution caused by oil sludges, many programs aim to treat the sludge in a manner that allows the oil to be extracted from the sludge. The main strategy to properly treat the sludge is to recover the valuable oil and dispose of the remaining fractions (Jerez et al., 2021; Johnson & Affam, 2019). A waste management strategy based upon the 3 R's processes: reduce, reuse, and recycle should be applied to manage oil sludges. Management of this waste includes employing technologies to reduce the production of waste from the petroleum industry, reutilization of waste without treatments that alter the waste's physiochemical characteristics, and recycling of the raw material that composes the waste (da Silva et al., 2012; Hu et al., 2013).

A limitation of the treatment options used nowadays is caused by the complex composition of the sludge. Crude oil sludge cannot be considered generic, so each treatment option needs to be specific for each type of sludge. This causes the treatment of this wastes to be challenging and time consuming. Several treatment options are based on chemical demulsification of the sludge. The phase separation facilitates the process of recycling the separated phases, which include oil, water, and solids. Most studies on the demulsification of oil sludge have been conducted

with simulated petroleum emulsions at laboratory scale. In this study, the demulsification will be conducted with real crude oil sludges. The results obtained from this research will help better understand how to efficiently separate crude oil sludges into three phases. By obtaining a successful three-phase separation, it is possible to reduce the amount of waste sent to further treatment facilities. The main goal is to receive a clean oil phase of good quality which could be successfully reused. New requirements from Equinor Mongstad Refinery require less than 1% water and solids in the oil. Proper treatment will also reduce costs related to chemicals, energy consumption, logistics and storage.

1.2 The purpose for the project

The aim of this thesis is to investigate the destabilization of crude oil sludges. The goal is to achieve a successful demulsification of the sludge, which separates the sludge into an upper phase, a middle phase, and a bottom phase of its three main components: oil, water, and solids, respectively. The goal includes identifying those conditions (dosage, temperature, and pH) that allow for the best separation. The main objective of the separation is to get oil in the upper phase that meets Equinor's refinery standard of less than 1 % water and solids. The three-phase separation enhances the treatment process of the waste as it allows each phase to be efficiently handled. This thesis provides a detailed insight into the destabilization process of oil sludges under different conditions, based on both literature study and laboratory experiments.

The laboratory experiments in this thesis investigate the demulsification of oil sludge in various conditions, such as chemical dosage, temperature, and pH. MudSplit chemicals and a polymer (N-Sep) are used to promote destabilization of the sludge, and the chemicals are provided by Norwegian Technology AS. The study is performed on crude oil sludge obtained from companies. Findings in this study can be transferred from the laboratory and applied in the field in a full-scale situation.

This thesis is presented as a novelty feature, as the study differs from previous studies where the efficiency of MudSplit chemicals was investigated on drilling fluids. The novelty of this study refers to implementing MudSplit chemical to such a complex waste type as crude oil sludges, which has limited experimental data on effective treatment processes.

1.3 Norwegian Technology AS

This project was initiated by the large interest of the Norwegian Technology AS in how to establish better waste management for crude oil sludge waste, based on the dialog with larger oil and gas (O&G) players who face this problem directly. It is assumed that one ton of oil sludge is produced for every 500 tons of crude oil processed in the refinery (Jerez et al., 2021), and more than one billion tons have accumulated worldwide (NorwegianTechnology, 2016).

Norwegian Technology AS is an international provider for the offshore and onshore industry that offers professional and sustainable treatment technologies. By introducing a complete treatment package, the waste management for crude oil sludges could be efficiently handled. Norwegian Technology offers an efficient treatment package, and an overview of the treatment process is presented in Figure 1.

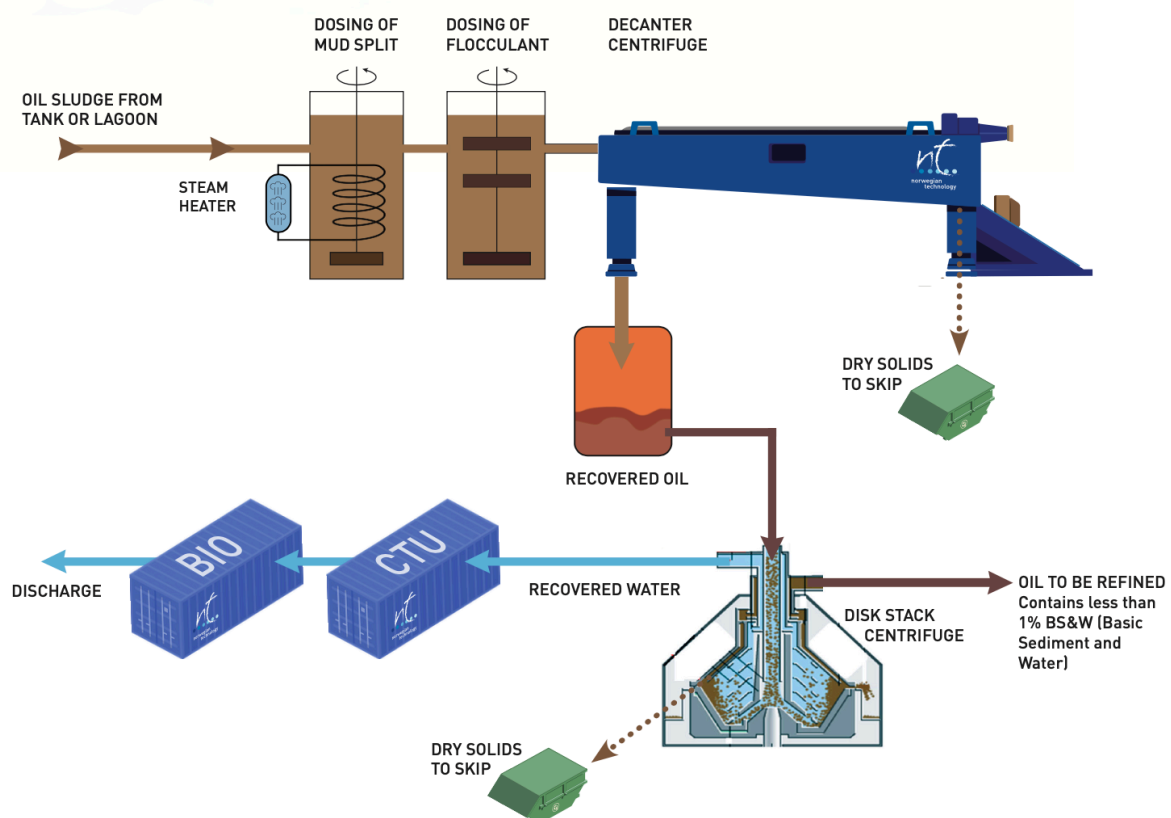


Figure 1 A complete treatment package from Norwegian Technology AS. Figure is from (NorwegianTechnology, 2016). The package includes mixers, heaters, and centrifuges for chemical and mechanical separation.

In the treatment process in Figure 1, the sludge is first destabilized by additions of chemicals. The destabilization is further enhanced by applying heat. Then the sludge is centrifuged by a

decanter centrifuge. Dry solids are skipped while the recovered oil is further separated in a disk stack centrifuge. The separated water is recovered, dry solids are skipped, and the oil can be refined. This thesis focuses on the destabilization of sludge by finding optimal conditions for the chemical treatment before centrifugation. The first step in Figure 1 (including dosing of chemicals and centrifugation) is performed during the laboratory work in this thesis.

1.4 Limitations for research

One limitation of this study was the low sampling volume of crude oil sludges. Difficulties in receiving sludge from suppliers made the sampling restricted. The low sampling volume limited the methodology and the experimental setup. Because the number of samples that could be performed was limited, several factors were tested in one sample. This could affect the results because the effect of some tested factors could not be separated from the effect of another factor.

1.5 Framework of the project

This thesis is structured as followed:

Chapter 2 includes a literature review on crude oil sludge, including its characterization, composition, and its environmental fate. This section focuses on the emulsion properties and the method for demulsification for handling the sludge.

Chapter 3 includes the methodology of the laboratory work. This chapter describes the different methods used in the experiment for the different types of sludges.

Chapter 4 includes the experimental results found for Mongstad sludge and Brenda sludge during the laboratory work. The results section is divided into pre-screening and main experiment.

Chapter 5 includes a discussion of the results, and suggested solutions on how to better optimize the recovery of crude oil.

Chapter 6 includes a summary of the results and conclusions based on the work done in this project. This chapter is followed by Chapter 7 where points for further research are stated.

At the end of this thesis, appendixes are presented.

2. Literature review

This chapter presents a brief review of crude oil sludge and its composition. Special focus is on the emulsion and demulsification properties of the sludge, which forms the basis for further study.

2.1 Oil sludge source

The upstream and downstream operations in the petroleum industry both generate a large volume of oily wastes. The upstream operation involves the processes of extracting, transporting, and storing of crude oil. The downstream operation refers to crude oil refining processes (Islam, 2015; Niven & McLeod, 2009).

The primary source of crude oil sludge includes oil storage tank sludge and oil sludge accumulated from refining processes (Shie et al., 2004). The accumulation of sludge in the oil tank causes a negatively impact on both the storage capacity and the safe operation of the oil tank (Jiang et al., 2021). Preceding being refined to petroleum products, crude oil is temporarily stored in storage tanks where it tends to separate into heavier and lighter petroleum hydrocarbons (PHCs) (Hu et al., 2013). The heavier PHCs settle at the bottom along with solid particles and water. This problem is aggravated by cool temperatures, the venting of volatile components from the crude, and by the static condition of fluid during storage (Heath et al., 2004). This mixture of the heavy ends that separates from the crude oil, solids, and water deposited at the storage tank bottom is known as oil sludge (Heath et al., 2004; Hu et al., 2013).

2.2 The composition of crude oil sludge

The composition of oil sludge is complex. It is a stable emulsifying dispersion system characterized as a water-in-oil (W/O) or oil-in-water (O/W) emulsion, which is composed of water, crude oil, petroleum hydrocarbons (PHCs), suspended solids, and metals (Islam, 2015; Jing et al., 2011; Li et al., 2020). The pH value usually ranges between 6.5 and 7.5 (Li et al., 2020). Total petroleum hydrocarbon (TPH) content of the sludge range from 15-50% (w/w), whereas water and solid contents are in the range of 30-85% and 5-46%, respectively (Jerez et al., 2021; Li et al., 2020).

2.2.1 Main components of crude oil

The composition of oil sludge varies depending on the crude oil source (type of production reservoir, geology and location), processing design, storage conditions, and equipment and reagents used in the refining process (Hu et al., 2013; Hui et al., 2020; Jerez et al., 2021). The components of crude oil consist of a percentage of dissolved gases, liquids, and solids (suspended and dissolved). The main components include aliphatic hydrocarbons, aromatic hydrocarbons, asphaltenes, resins, and some nitrogen, sulfur, and oxygen (Hui et al., 2020; Li et al., 2020; Ubani et al., 2013). The liquids are generally divided into saturates, aromatics, and resins, whereas the most prominent solids in crude oil are solid asphaltene (Fakher et al., 2020; Goel et al., 2016).

The saturates are often referred to as paraffins or alkanes and are the compounds in the hydrocarbon that are saturated (do not contain any double bonds) (Fakher et al., 2020). This fraction contains mostly aliphatic compounds (Akmaz et al., 2011). Compounds ranging from methane through butane are gaseous at room temperature, whereas compounds ranging from pentane through heptadecane are liquids. The heavier members of the paraffins are categorized as wax-like solids. Examples of some general saturates are presented in Figure 2. The aromatics are characterized by an unsaturated hydrocarbon ring with multiple carbon-carbon double bonds within the ring configuration (Fakher et al., 2020). Aromatics are generally nonpolar, but their molecule may consist of polar functional groups. The aliphatic and aromatic hydrocarbons constitute the largest part of PHCs in oil sludge (Hu et al., 2013). Their most prevalent compounds include alkanes, cycloalkanes, benzene, toluene, xylenes, naphthalene, phenols, polycyclic aromatic hydrocarbons (PAHs), and other volatile and refractory organic compounds (Hu et al., 2013; Hui et al., 2020). Examples of some general aromatics are presented in Figure 3.

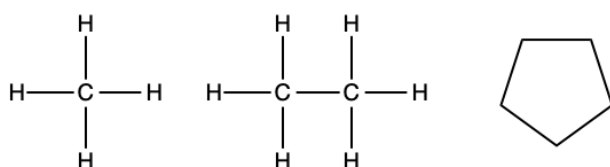


Figure 2 Molecular structure of methane, ethane, and cyclopentane, respectively.

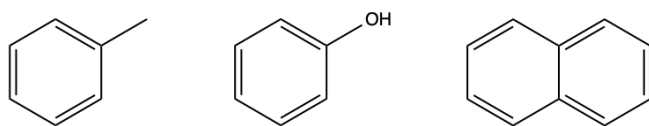


Figure 3 Molecular structure of toluene, phenol, and naphthalene, respectively.

Naphthenic acids (NAs) are a class of cycloaliphatic carboxylic acids which are present in crude oil. NAs have an empirical formula of $C_nH_{2n+z}O_2$, where n is the number of carbon and z specifies a homologous series. The definition of NAs has been extended, and today it refers to all of the carboxylic acids present in petroleum, including acyclic, aromatics and those containing heteroatoms such as nitrogen and sulfur (Havre et al., 2003; Yang et al., 2019). The majority of NAs comprises of 10 – 50 carbon atoms (Havre et al., 2003), one example is presented in Figure 4. They are weak acids that have pKa values of approximately 5 to 6 (Petroleum HPV Testing Group, 2012). The smallest molecules of NAs are quickly dissolved in the aqueous phase, while the larger molecules tend to be more oil soluble. However, most of these homologues can be dissolved in an aqueous phase at elevated pH (Havre et al., 2003), while some NAs do not turn into salts even at high pH (Hurtevent et al., 2006).

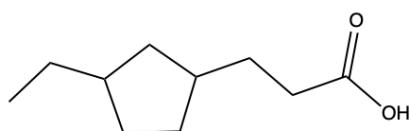


Figure 4 Example component of naphthenic acid (3-(3-ethylcyclopentyl)propanoic acid).

Compared to saturates and aromatics, resins are considered more complex. Resins contain heteroatoms such as nitrogen, oxygen and sulfur (Yonguep et al., 2022). Their chemical structure is similar to asphaltenes but has lower molecular weights. Resins function as a bridging material which connects the nonpolar hydrocarbons to the polar asphaltene, as resins have both a polar and a nonpolar side (Fakher et al., 2020). An example of a typical resin compound is presented in Figure 5.

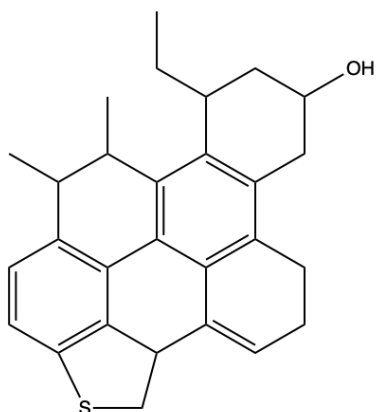


Figure 5 Molecular structure of a typical resin compound.

Asphaltenes are usually highly polar compared to crude oil, which generally is nonpolar. Asphaltene is one of the most complex components in crude oil, consisting of many different structures, making it difficult to generalize (Fakher et al., 2020). To this date, asphaltene is defined as “the heaviest components of petroleum fluids that are insoluble in light n-alkanes such as n-pentane or n-heptane but soluble in aromatics such as toluene” (Goual, 2012). Some characteristics can be used to identify asphaltenes, including (Fakher et al., 2020; Yonguep et al., 2022):

- Solid: asphaltene is a solid phase homogenized in crude oil under reservoir conditions.
- n-Alkane insoluble: it is the highest molecular weight (500 – 1500 gmol⁻¹) component in the crude oil that is insoluble in light n-alkanes (as n-pentane or n-heptane) and soluble in aromatics (as toluene or xylene).
- Highly polar: it is one of the few components of crude oil that is highly polar in contrast to crude oil, which is considered nonpolar.
- Heteroatoms: asphaltene is associated with heteroatoms, mainly nitrogen, oxygen, and sulfur.

Asphaltene is stable under reservoir thermodynamical conditions and thus, remains stable in the oil until a disturbance of its equilibrium occurs (Fakher et al., 2020). By disturbance of its equilibrium, asphaltene can form solid particles inside the crude oil, which could cause precipitation of solid asphaltene from the crude oil solution (Fakher et al., 2020). Figure 6 presents the most widely accepted asphaltene model nowadays. The model describes the

structure of asphaltene based on its size and behavior as a function of its concentration in the crude oil (Fakher et al., 2020; Mullins et al., 2013)

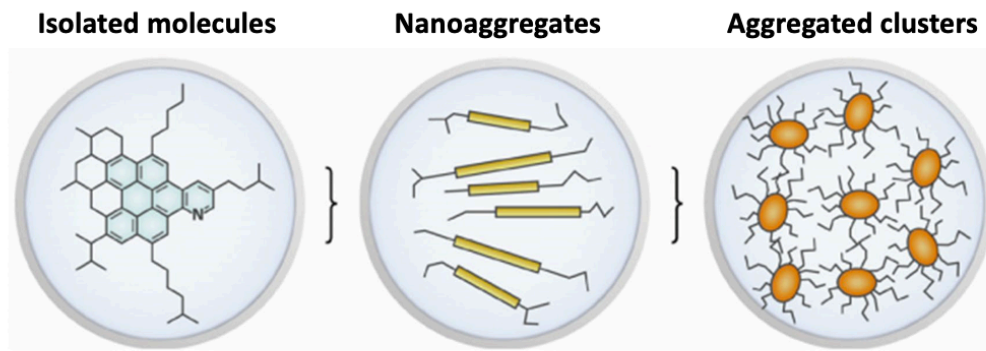


Figure 6 Yen-Mullins asphaltene model (Mullins et al., 2013). The model provides an understanding of the asphaltene molecule and its size. At low concentrations asphaltene will be present as isolated molecules, while at higher concentrations it will begin to form aggregates and clusters.

Oily sludge generally comprises 28-33% aromatics, 40-55% alkanes, 8-12% asphaltenes, and 10-22.4% resin (Li et al., 2020). According to recent research, high concentration of the metals zinc (Zn), iron (Fe), copper (Cu), chromium (Cr), nickel (Ni), and lead (Pb) was reported in oil sludge from refineries (Johnson & Affam, 2019; Ramirez et al., 2021).

The physicochemical properties such as density, viscosity, and heat value of oil sludge can vary significantly due to the diverse chemical composition (Hu et al., 2013). Consequently, the properties measured from one oil sludge source are not equal to those from another.

2.3 Rheological properties of oil sludge

Rheology is the study of the flow and deformation of matter. The term describes the deformation (also called strain) of a material as a result of applied force, the stress (Barnes & Gentle, 2011). Although stress can take on various forms, it is the shear stress that is of interest in terms of rheology. The rheological behavior of fluids is divided into Newtonian and non-Newtonian. Newtonian fluids are associated with ideal behavior, where the shear stress is linearly proportional to the time rate of the strain ($\frac{dy}{dt}$) (Barnes & Gentle, 2011). The proportionality constant is called the viscosity (μ). Newton's law of viscosity (in differential form) describes the shear stress (τ) by equation 1:

$$\tau = \mu \frac{d\gamma}{dt}$$

Equation 1

For non-Newtonian fluids, the shear stress is not linearly related to the strain rate. Non-Newtonian fluids can be divided into two main types; shear thinning (or pseudoplastic), where the viscosity decreases with increased shear rate, and shear thickening (or dilatant), where the viscosity increases with increased shear rate (Barnes & Gentle, 2011). The rheological description of oil sludge is problematic due to its varying composition and complexity. The relatively high content of solid particles and water significantly affects its rheological properties. There are many terms connected to the study of rheology, but only viscosity is in the focus of this thesis.

Viscosity

Viscosity measures a fluid's resistance to deformation or flow by applied shear stress. It describes the internal friction of a moving fluid and, therefore, its thickness. The viscosity of crude oil sludges can vary greatly depending on their composition. The viscosity of the continuous phase (which can be either water or crude oil) provides the viscosity for the sludge system. The viscosity of the sludge system is also strongly affected by solid particles, droplet size and volume of the dispersed medium.

The rheological properties of crude oil sludges vary based on several factors, which include many variables. Describing its rheological behavior is therefore challenging. Despite the lack of literature describing the viscous behavior of oil sludge, some scientists describe it as a shear-thinning non-Newtonian fluid (Heath et al., 2004; Jie et al., 2015; Souas, 2022). However, each sludge needs to be tested individually to get reliable data.

Stokes law

Stokes law is a mathematical equation that can be used to express the settling velocity of small spherical particles (or droplets) in a fluid medium by gravity separation (Equation 2) (Gregersen, 2021). Gravity separation is driven by density differences between the continuous and the dispersed phase, and increased separation can be accomplished by manipulating the viscosity, droplet size or gravitational force. However, the law is only valid under ideal conditions, which include: (1) laminar flow (Reynolds number < 1), (2) spherical

particles/droplets, (3) particles/droplets are of the same size and (4) particles/droplets should not interact with each other.

Stokes law is used in gravity separators in the petroleum industry to treat different petroleum emulsions, such as oil sludge. The settling velocity described by Stokes law can be calculated by Equation 2:

$$V_s = \frac{gd^2(p_1 - p_2)}{18\mu} \quad \text{Equation 2}$$

Where V_s is the settling velocity [ms^{-1}], g is the constant for gravitational acceleration [9.81 ms^{-2}], d is the droplet diameter [m], p_1 the density of the continuous phase (water) [kgm^{-3}], p_2 the density of the dispersed phase (oil) [kgm^{-3}] and μ the viscosity of the continuous phase (water) [$\text{kgm}^{-1}\text{s}^{-1}$ or Nsm^{-2}].

When Stokes law is used in equipment like centrifuges and hydrocyclones, where the settling of particles is forced to spin in a circular path with a higher gravitational force, the law of settling is extended by Equation 3.

$$a_c = \frac{V_T^2}{r} = \frac{(r\omega)^2}{r} = \omega^2 r \quad \text{Equation 3}$$

Where a_c is the centripetal acceleration [ms^{-2}], V_T the tangential velocity [ms^{-1}], r is the radius of circular path [m] and ω the angular velocity [s^{-1}].

By replacing the gravity constant in Stokes law (Equation 2) with the centripetal acceleration (Equation 3), the equation can be used to determine the settling velocity in hydrocyclones or centrifuges (Equation 4).

$$V_s = \frac{d^2\omega^2 r(p_1 - p_2)}{18\mu} \quad \text{Equation 4}$$

Higher separation efficiency can be achieved by manipulation of Stokes law. This can be done by reducing the viscosity of the suspended fluid, increasing the droplet size, or increasing the gravitational force.

A briefer description of how Stokes law is used in the separation process of oil, water, and solids is described in the later chapter under physical or mechanical demulsification.

2.4 Internal structure of crude oil sludge

In order to describe and understand crude oil sludges, it is necessary to illustrate the internal structure of the sludge system. The internal structure may vary depending on its composition, which could affect the properties of the sludge.

2.4.1 Emulsions

An *emulsion* is defined as a dispersion (of droplets) of one liquid in another immiscible liquid medium. The phase that is present as droplets is the dispersed or internal phase, and the phase in which the droplets are suspended is the continuous or external phase. Emulsions are usually thermodynamically unstable. This is because droplets of the same liquid tend to coalesce to reduce the interphase's surface area and, as a result, separate into two phases (Barnes & Gentle, 2011). Emulsions are usually stabilized by emulsifiers or surface-active agents (surfactants). Generally, emulsions fall into two categories: oil-in-water (O/W) and water-in-oil (W/O), as shown in Figure 7. Whether an O/W or W/O emulsion is formed depends on several factors, such as the ratio of oil to water, another is the emulsifier used (Barnes & Gentle, 2011). The constituent with the higher phase volume has a propensity to form the continuous phase.

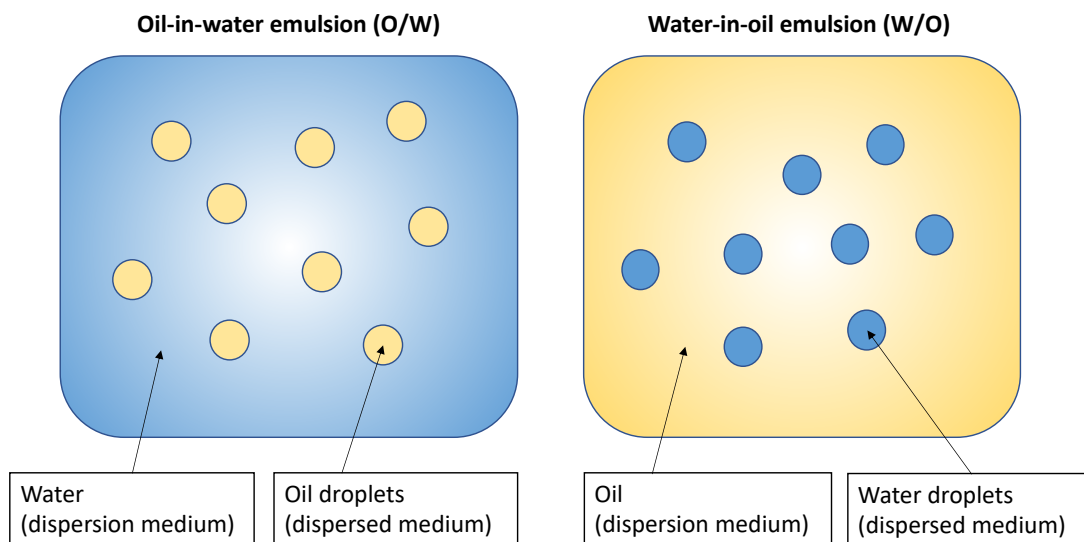


Figure 7 Main types of emulsions, oil-in-water (O/W) and water-in-oil (W/O)

Emulsions can also be categorized into multiple or complex emulsions. These emulsions are oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W) (Dhandhi et al., 2021; Saad et

al., 2020), as presented in Figure 8. These emulsions consist of droplets dispersed in bigger droplets suspended in a continuous phase.

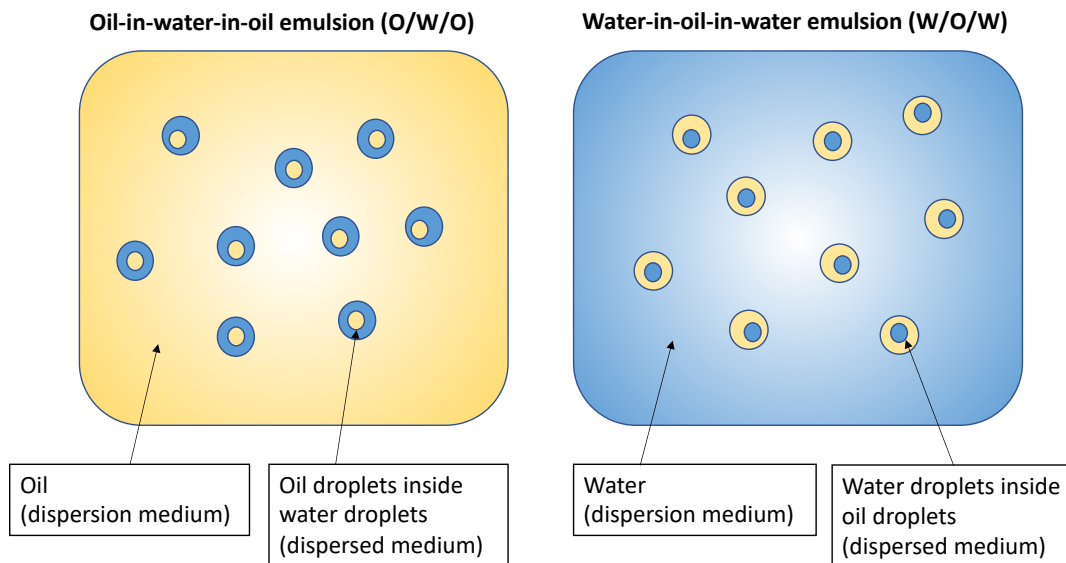


Figure 8 Multiple or complex emulsions, oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W)

Emulsifiers

Emulsifiers stabilize the emulsion by reducing the interfacial tension at the oil-water interface. This is because the emulsion droplets surface gets coated with an adsorbed layer of the emulsifier, which hinders droplet coalescence. Two static effects describe this: “one is the reduction of interfacial tension caused by the emulsifier and the consequent decrease in the thermodynamic drive towards coalescence; the other is the physical barrier that the adsorbed layers impose” (Barnes & Gentle, 2011). Emulsifiers can include both surface-active agents (surfactants) and finely divided solids. *Surfactants* are compounds known as amphiphiles, meaning that the molecule consists of one hydrophilic and one hydrophobic part. The balance between the hydrophobic and hydrophilic parts can vary considerably, and this balance is referred to as the hydrophilic-lipophilic balance (HLB) (Barnes & Gentle, 2011). Surfactants can be divided into four classes based on the ionic nature of the hydrophilic part: anionic, cationic, non-ionic, and zwitterionic (amphoteric) (Barnes & Gentle, 2011). The four classes of surfactants are illustrated in Figure 9.

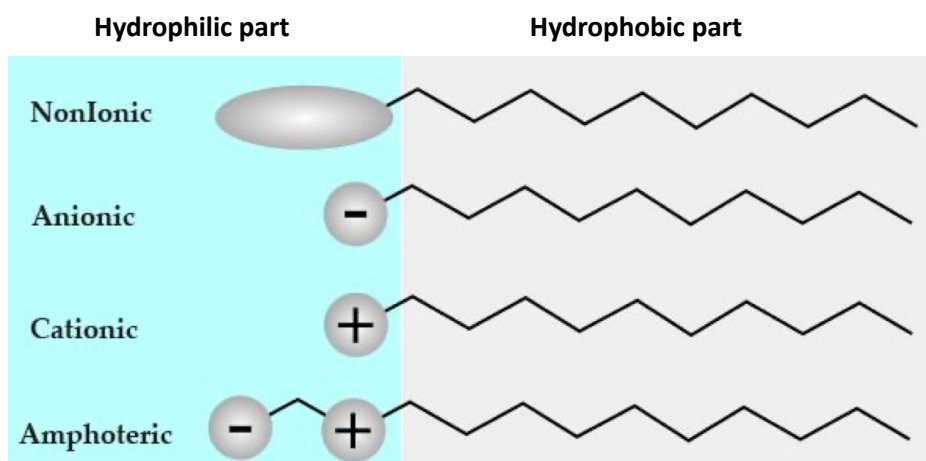


Figure 9 Classification of surfactants and their hydrophilic and hydrophobic parts. Figure is adapted from (Dave & Joshi, 2017).

2.4.2 Emulsion formation

A considerable problem in the petroleum industry is the abundance of water that accompanies the extraction of crude oil. Emulsions can be formed spontaneously but are more often formed by mechanical dispersion, such as agitation. In the production process, three factors are responsible for the formation of an emulsion. These factors are turbulent flows, increased pressure through valves, and vibratory movements of oil during transport in pipelines or tanks (Saad et al., 2020). Three key factors must be available in the formation of a stable emulsion: (1) Two (or more) immiscible liquids need to be in contact, (2) the presence of an emulsifier, and (3) significant agitation or shear (Saad et al., 2020). These factors result in the mixing of the immiscible liquids and the emulsifier. The emulsifier's presence, proportion, and nature largely determine the emulsion's type and stability. Crude oil contains natural emulsifiers, which is why crude oil may form such stable emulsions.

2.4.3 Emulsion stability

The stability of emulsions is dependent on the rheological properties of the system. It is mainly caused by the strong interfacial network surrounding the droplets, which prevents them from coalescing (Yonguep et al., 2022). Several factors influence the formation and stability of oil sludge emulsions. Factors such as droplet size, viscosity, presence of solid particles, and functional molecules such as NAs, asphaltenes and resins have an essential impact on the emulsion stability.

Surfactants

Surfactants are surface-active molecules that can reduce the interfacial tension between two immiscible liquids (Yonguep et al., 2022). Its amphiphilic nature causes it to be positioned at the emulsion interface, at the oil-water interface. Crude oil contains several components which act as natural surfactants and affect emulsion formation and stability to different degrees.

Adsorption and desorption take place when the surfactant molecules are in solution. Adsorption at the oil-water interface causes lower interfacial tension, higher surface elasticity and electric double layer repulsion (Yonguep et al., 2022). In addition, it can possibly increase the surface viscosity of the emulsion and consequently affect the stability.

Viscosity and droplet size

The stability is highly dependent on the viscosity of the emulsion, in particular the viscosity of the interfacial film (Yonguep et al., 2022). Increased viscosity reduces the film's drainage rate during droplet coalescence. This is because of the formation of a repulsive force that hinders the droplets breakdown (Yonguep et al., 2022).

The viscosity of an emulsion is dependent on the average droplet size and size distribution (Barnes & Gentle, 2011; Pajouhandeh et al., 2016). An emulsion consisting of small droplets of the dispersed phase will contribute to the high viscosity of the continuous phase and stabilize the emulsion (Saad et al., 2020). Also, emulsions consisting of smaller droplets are shown to be more challenging to separate than those consisting of larger droplets, as it takes longer for the smaller droplets to coalesce (Dhandhi et al., 2021; Yonguep et al., 2022). The droplet size may be influenced by high shear rates (rapid mixing), which facilitates the breaking up of the droplets into smaller droplets (Yonguep et al., 2022). In general, emulsions with smaller droplet sizes and smaller size distribution tend to be more viscous due to friction increment (Pajouhandeh et al., 2016). The presence of solids and high molecular weight compounds may additionally increase the viscosity as it affects the properties of the interfacial film.

Stabilization by solids

Finely divided solid particles may further stabilize the interfacial film of the emulsion. These particles could include sand, suspended solids in the seawater, suspended sediments, salts, and other small particles (Yonguep et al., 2022).

After the emulsion has formed, the particles move to the oil-water interface and are wetted by both oil and water, resulting in increased stability (Barnes & Gentle, 2011). The solid particles raise the rigidity of the interfacial film and inhibit the emulsion droplets from coalescence (Dhandhi et al., 2021). The stabilization of particles is affected by the particle size, wettability, and interactions of particles with emulsions (Dhandhi et al., 2021).

Functional molecules

Inorganic solids and functional molecules like NAs, paraffin wax, asphaltenes and resins are found to contribute to the stabilization of crude oil emulsion (Dhandhi et al., 2021; Saad et al., 2020; Yonguep et al., 2022). NAs, asphaltenes and resins are natural components found in the heavy fraction of the crude oil, which has surfactant properties.

NAs and their salts, called naphthenates, are surface-active and will accumulate at the oil-water interface (Havre et al., 2003). The strong surfactant capacity of NAs and naphthenates are dependent on the nature of the NAs present in the oil. The emulsion problems associated with NAs usually generate discharge water with high hydrocarbon and naphthenate content (Hurtevent et al., 2006). The high hydrocarbon content is due to the amphiphilic nature of the NAs, causing the naphthenates to carry hydrocarbons into the water (Hurtevent et al., 2006).

The high stability of oil sludge emulsions is thought to be due to the presence of amphiphilic substances, such as asphaltenes and resins, which act as lipophilic emulsifiers (Rondón et al., 2006). Several researchers state that asphaltene and resins are the main contributing factors to stabilizing W/O emulsions, even at low concentrations (Dhandhi et al., 2021; Fingas, 1995). The presence of wax can contribute further to the stabilization of W/O emulsions. Crude oils low in asphaltenes and high in wax can form emulsions stabilized by the rheological strength of the continuous phase (due to precipitated wax) rather than chemical stabilization of asphaltenes and resins (Moldestad et al., 2006; Sjöblom, 2006).

Asphaltene molecules tend to aggregate at the oil-water interface to form a viscoelastic and physical cross-linked network to prevent droplets from coalescing (Yonguep et al., 2022). This can also function as a steric layer to promote steric stabilization of the emulsion. Resins do not form aggregates and exist as a single molecule on the interfacial film (Yonguep et al., 2022). This makes the interfacial film formed by resins weak and could be easily broken by weak shear

forces. Resins adsorb to the asphaltene molecules and make them soluble, but they can also desorb from asphaltene leading to larger asphaltene aggregates (Yonguep et al., 2022).

A study by J. Zhang et al. (2016) describes how asphaltene can be adsorbed at the oil-water interface and form an ordered structure interfacial film that stabilizes the W/O emulsion. It is also described how resins contain surface-active materials that can form a structured interfacial film that stabilize the O/W emulsion (J. Zhang et al., 2016). Another study by Yarranton et al. (2007) describes how asphaltene aggregates adsorb to the interface and form a solid layer on the surface that stabilizes the emulsion and acts as a mechanical barrier to coalescence (Saad et al., 2020). There is a general agreement among scientists that the stable interfacial film formed by asphaltenes and resins prevents the dispersed droplets from colliding and coalescing and, as a result, stabilizes the emulsion. The mechanism of asphaltene stabilization is illustrated in Figure 10.

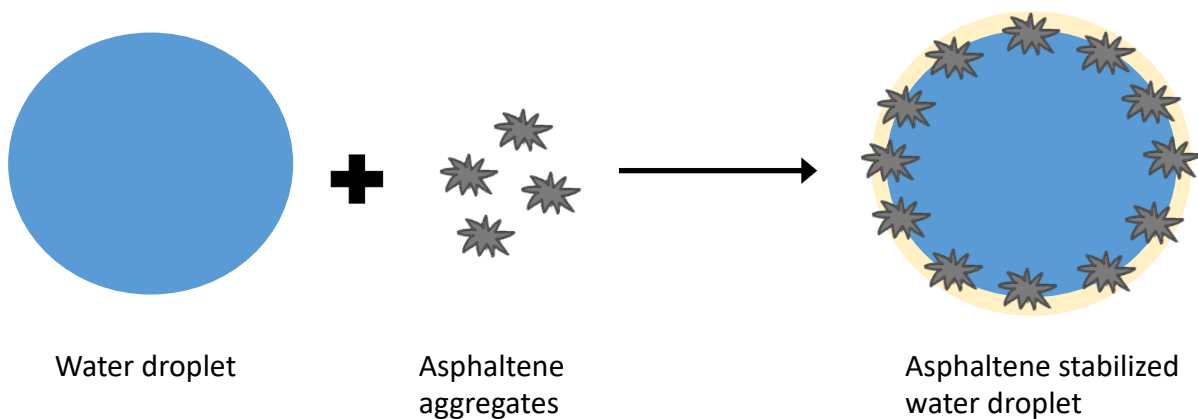


Figure 10 Illustration of emulsion stabilization by asphaltenes. Asphaltene aggregates form a thin layer around the dispersed water droplet to provide steric stabilization of the emulsion. Figure is adapted from (Yonguep et al., 2022).

2.5 Demulsification

Demulsification is the process where emulsions are broken down into their initial phases. The separation of an emulsion occurs in two stages: flocculation and coalescence. The first step of demulsification is flocculation. Flocculation occurs when the emulsion droplets cluster together, forming aggregates or flocs, without merging (coalescence) (Barnes & Gentle, 2011). This can arise from the density difference between oil and water and can cause the oil droplets in an O/W emulsion to rise to the surface in a process called creaming, or the water droplets to fall to the bottom called sedimentation (Barnes & Gentle, 2011). Under flocculation, the

distance between the droplets of the dispersed phase decreases due to the weakening of the net attractive force between them (Yonguep et al., 2022). At this stage, coalescence only occurs if the emulsifier film surrounding the droplets is significantly weak. The second step in demulsification is coalescence. Coalescence occurs when the emulsion droplets merge or coalesce to form a larger drop. During coalescence, the thin interfacial film separating the dispersed droplets is eliminated (Yonguep et al., 2022). This process results in a decrease in the total amount of droplets, eventually leading to a complete demulsification. The demulsification mechanism is shown in Figure 11, in which flocculation, creaming, sedimentation and coalescence take place.

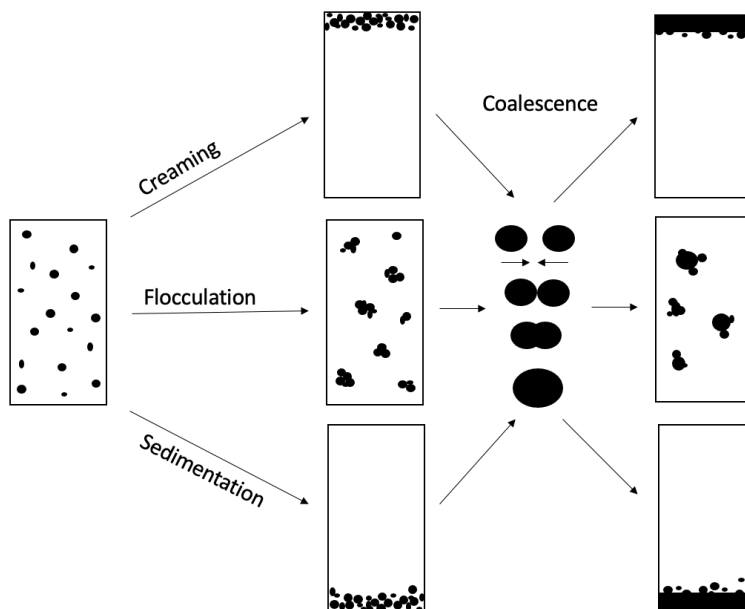


Figure 11 Illustration of the demulsification mechanism. Creaming and sedimentation occur because of the droplets natural tendency to rise or sink under the influence of gravitational forces and density differences. Figure is inspired and adapted from (Dhandhi et al., 2021).

The flocculation rate depends on water cut, temperature, the viscosity of the continuous phase and density differences. The coalescence rate depends on flocculation rate, interfacial film strength, interfacial tension, viscosity and temperature (Yonguep et al., 2022).

Two main demulsification techniques are chemical and physical. The chemical approach includes applying suitable chemicals, called demulsifiers, to the emulsion to promote demulsification. The physical approach includes heating, electrical or mechanical treatment

(Saad et al., 2020). Heating is often also included during chemical treatment. The electrical approach will not be described further in this thesis.

2.6 Demulsification techniques of crude oil sludge

Effective demulsification requires the rate of phase separation to be fast. The process should be inexpensive and easy to operate. In the following chapters, physical and chemical demulsification techniques are described.

2.6.1 Physical or mechanical demulsification

Mechanical demulsification is a method where emulsions are separated utilizing mechanical equipment such as centrifugal separators, cyclones or gravity settling tanks (Yonguep et al., 2022). The proportion of solid particles and water influence the density and viscosity of crude oil sludges. Hydrocyclones are installed in almost every offshore installation where space is limited and is widely used to separate oil and water (Belaidi & Thew, 2003). Hydrocyclones have a fixed cone (body) for the separation and no moving parts and therefore have lower maintenance costs (Sabbagh et al., 2015). Decanter centrifuges are typically applied in the processing and treating of oil sludge and waste oil (Hiller GmbH, 2022), consisting of a significant amount of solid particles and water. However, centrifuges can be associated with high energy consumption due to the high gravitational forces. High maintenance costs and high wear rate are other disadvantages of this type of centrifuge (Sabbagh et al., 2015).

Hydrocyclone

Hydrocyclones have been widely used since the mid-1980s in oil-water separation (Belaidi & Thew, 2003) and is an efficient way to separate slurries. They are generally used as the final step in the separation process of produced water but can be used to separate emulsified slurries like oil sludge (Huang et al., 2020). Hydrocyclones separate solids or fluids with different densities from the bulk fluid. The centrifugal acceleration range between 500 and 5000 g, depending on design and operation conditions (Davailles et al., 2012). Cyclones comprise four main sections: (1) cylindrical-shaped feed chamber, (2) cone (body), (3) underflow (spigot liner or apex) and (4) overflow (vortex finder). The feed chamber is designed to transfer the slurry into a spiral, creating a vortex. The cone is designed to allow the slurry to continue spiraling at a higher velocity, generating a centripetal force. The underflow is the bottom of the cyclone and where the denser particles/fluids exit. The overflow is the top of the cyclone and where the

less dense particles/fluids leave (JasperEngineering, 2020). A simplified separation principle for hydrocyclones is presented in Figure 12.

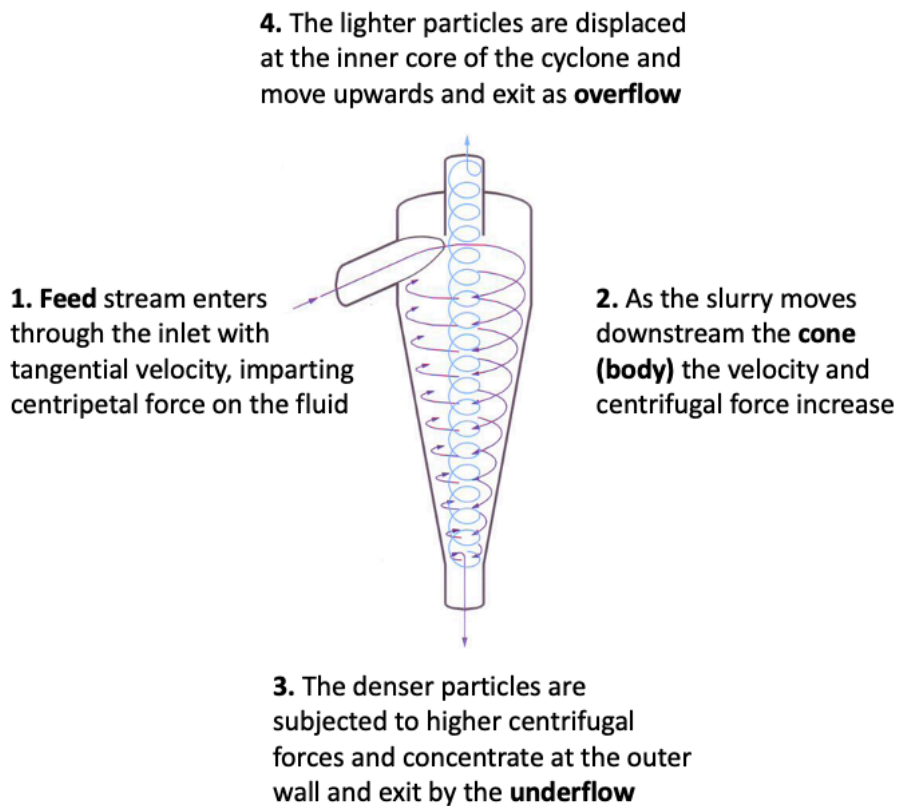


Figure 12 Hydrocyclone separation principle. The movement of the inlet feed stream is marked as 1, the cone (body) marked as 2, underflow marked as 3 and overflow marked as 4. The working principle follows Stokes law and its conditions.

Decanter centrifuge

A decanter centrifuge provides a liquid-solid separation technology in which solid materials are separated from a liquid sludge slurry. The centrifuge can reach accelerations of up to 4000 g, in which the solids are separated from the liquids (Hiller GmbH, 2022). The separation follows Stokes law because the high centrifugal force creates a laminar flow. Consequently, solids settle to the side. During settling, solids with higher density settle first. Figure 13 illustrates a decanter centrifuge and its components provided by Norwegian Technology.

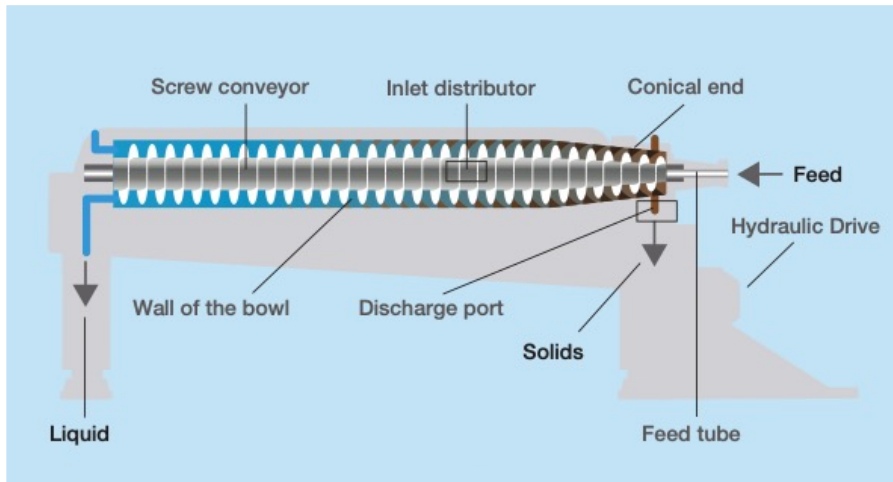


Figure 13 Decanter centrifuge (Hiller decanter centrifuge) provided by Norwegian Technology AS (NorwegianTechnology, 2016). The sludge is pumped into the feed tube and into the rotational horizontal bowl. Under high centrifugal forces, solid particles (higher density) are collected at the wall of the bowl (according to Stokes law). The screw conveyor rotates inside the bowl at a slightly different speed (called the differential speed), which causes the settled particles to be moved to the end conical part and be discharged via the discharge port. The separated liquid (lower density) is discharged at the opposite end of the decanter, in the liquid discharge zone (Flottweg, 2022)

Depending on which slurries are to be treated, pretreatment is often necessary. If crude oil sludges are to be treated, pretreatment is often crucial in achieving efficient and optimal separation. Pretreatment can consist of thermal treatment or chemical dosing, as viscosity, temperature and, density differences influence the separation efficiency.

The separation of solids from oil sludge by mechanical equipment is essential to reduce its viscosity. The separation of fluids with different densities (oil and water) is also necessary to get clean phases that can be reused or discharged in an environmental manner. Both decanter centrifuges and hydrocyclones are based on the fundamental understanding and manipulating of the process based on Stokes law.

2.6.2 Chemical demulsification

Chemical demulsification is a method where demulsifiers (a group of chemicals or surfactants) are added to the emulsion to accelerate or promote demulsification. Demulsifiers neutralize the stabilization effect of surfactants by displacing them from the interfacial film surrounding the dispersed droplets (Yonguep et al., 2022). Chemical demulsification is affected by temperature, pH, salinity, water/oil content, demulsifier type, demulsifier dosage, retention time and ageing. Each variable has a different degree of effect on the demulsification process. High efficiency

can be obtained by involving a synergistic effect of one or more of these parameters (Saad et al., 2020). This research focuses on testing chemical destabilization as the primary method, and the main factors affecting the process are presented below.

2.6.2.1 Effect of temperature

Heat energy has an important impact on the demulsification process of crude oil emulsions. Heat energy reduces the viscosity of the continuous phase, which is beneficial for the gravitational settling separation (Dhandhi et al., 2021; Z. Wang et al., 2018). Reducing the viscosity facilitates the kinetic motion of the dispersed droplets, which can result in film relaxation, film rupture and coalescence (Al-Sabagh et al., 2015). Temperatures affect the physical properties of the oil-water interfacial films (Yonguep et al., 2022). Increasing the droplets thermal energy increase the collision rates between droplets, and this affects the stability of the emulsion. It decreases and destabilizes the oil-water interfacial films and makes it easier for the droplets to coalesce when colliding (Saad et al., 2020). However, using heat in the demulsification process could result in the evaporation of light hydrocarbons, which could affect the quality of the oil (Saad et al., 2020). In the industry, heating in combination with adding chemical additives (demulsifier), called a thermal chemistry process, is common as these two factors speed up the demulsification process (Saad et al., 2020). This is because heat strengthens the Brownian motion within the emulsion, which causes the fast movement of demulsifiers at the emulsion interface (Yonguep et al., 2022). Al-Sabagh et al. (2015) investigated how temperature affected the demulsification efficiency of W/O emulsions. Results showed that a rise in the temperature from 50 to 70 °C improved the demulsification efficiency (Al-Sabagh et al., 2015). L. Zhang et al. (2018) investigated the ratio of oil separation of O/W emulsions by using hyperbranched poly(amido amine) and studied the effect of temperature differences. The results showed a steady increase in the oil removal ratio with increasing temperatures from 30 to 60 °C (L. Zhang et al., 2018).

2.6.2.2 Effect of pH

The demulsification process is affected by pH and is correlated with the nature of the oil, salinity and organic acids in the emulsion (Dhandhi et al., 2021; Saad et al., 2020).

A system consisting of NAs combined with water and an oil phase will follow an acid-base equilibrium reaction in a multiphase system. Critical factors for this equilibrium are described

by (1) the partitioning coefficient, which describes the acid partitioning between the oil and water phases and (2) the dissociation constant (pKa), which describes the acid dissociation in the water phase (Hurtevent et al., 2006). However, the pKa value does not take into account the low solubility of NAs in the water phase.

NAs will partition between the oil and water phase according to Equation 5, where HA_O and HA_W represent the undissociated NA in the oil and water phase.



The equilibrium from Equation 5 can be described by a partition coefficient given by Equation 6:

$$K_{OW} = \frac{[HA]_W}{[HA]_O} \quad \text{Equation 6}$$

When the NA have been distributed into the water phase, the acid will dissociate in the water phase according to Equation 7. The equilibrium constant is given by Equation 8.



$$K_a = \frac{[A^-]_W [H^+]}{[HA]_W} \quad \text{Equation 8}$$

From a study done by Havre et al. (2003), it is observed that the undissociated form of NAs dominates at low pH. The undissociated form is also more oil-soluble and tends to stay in the oil phase. As the pH of the water phase increases, a significant decrease in the interfacial tension at the oil-water interface has been observed (Havre et al., 2003). At $pH > pK_a$, the dissociated form of NAs dominates in the water phase.

A general conclusion stated by Hurtevent et al. (2006) is that the emulsion stability is dependent on pH. Stabilization by naphthenates is dependent on the capacity of NAs to dissociate and form naphthenates at the lowest possible pH (Hurtevent et al., 2006). For some crude oils, the formation of naphthenates occurs from pH as low as 6.

The stabilization effect of functional molecules like asphaltene, resin and wax is believed to be affected by pH (Fortuny et al., 2007; J. Zhang et al., 2016). The interfacial films formed by asphaltene are shown to get weakened by rising pH levels and can be progressively more rigid

at lower pH (Dhandhi et al., 2021). In contrast, the films formed by resins are weakened at low or medium pH and increase in strength at high pH levels (Saad et al., 2020). In addition, if the surfactant is ionized at the interfacial film of emulsion, it can give a charge to single-phase droplets which may be positive or negative at low pH (Dhandhi et al., 2021). This ionization effect is impacted through saline solution because of the interaction between surfactant and salt molecules. A study done by Long et al. (2013) investigated the impact of pH on the efficiency of dewatering using the biosurfactant rhamnolipid. The results indicated that the effect of pH could be correlated with the type of emulsion (O/W or W/O). The results showed that in a W/O emulsion, a pH of 10 gave the best demulsification effect of 89%, while in an O/W emulsion, a pH of 3 gave a demulsification effect of nearly 100% (Long et al., 2013). Liang et al. (2015) investigated the demulsification efficiency of magnetic nanoparticles for cyclohexane-diluted crude O/W nanoemulsions and the impact of pH. The results showed that the demulsification efficiency remained stable in the pH range of 4.0 – 7.5 and decreased as the pH increased above 8.0 (Liang et al., 2015).

2.6.2.3 Effect of salinity

The presence of salts can significantly impact the emulsion because of the so called “salting effect” (Saad et al., 2020). The salting effect reduces the interaction between water and the surfactant (Martínez-Palou et al., 2013). Due to the presence of salt, the hydrophilicity of the surfactant is decreased by reducing the interaction with water at the interfacial film (Dhandhi et al., 2021). Jones et al. (1978) have mentioned that divalent ions stabilize emulsions by forming rigid films around the water droplets (AL-Doury, 2019). The water present in crude oil sludges is in the form of brine droplets, also called formation water (FW), which is associated with the O&G reservoirs. The salt concentration in FW may vary greatly, ranging from a few hundred to several thousand ppm (Anand & Thaokar, 2021). FW naturally exists in the rock before drilling (Anand & Thaokar, 2021) and contains various soluble organic and inorganic compounds. The ion composition of typical FW of four North Sea sandstone reservoirs is presented in Table 1. The unit mg/L is the unit of total salinity (or TDS), and “IS” is the ionic strength.

Table 1 Typical FW compositions of four North Sea sandstone reservoir. The table and its content is adapted from (Aghaeifar, 2019).

Ions	FW1 [mM]	FW2 [mM]	FW3 [mM]	FW4 [mM]
Na ⁺	355.2	939.5	2563.2	2842.2
K ⁺	1.6	17.8	58.8	144.3
Mg ²⁺	3.4	7.0	18.3	95.6
Ca ²⁺	12.2	44.2	123.8	753.1
Ba ²⁺	0.0	5.2	0.6	3.5
Sr ²⁺	0.0	3.0	0.9	12.4
HCO ₃ ⁻	0.0	7.7	3.4	1.3
Cl ⁻	387.9	1068.5	2905.7	4714.5
SO ₄ ²⁻	0.0	0.0	0.0	0.0
TDS [mg/l]	22 551	63 567	170 010	272 282
IS [M]	0.403	1.136	3.053	5.580
* Absolute concentrations of trace ions are uncertain				

Martínez-Palou et al. (2013) studied the demulsification effect of microwave and oil bath heating and the effect of a chemical demulsifier and salt content of an O/W emulsion. The results showed that water separation increased with microwave power and salt content in the presence of a chemical demulsifier (Martínez-Palou et al., 2013). However, salt-assisted microwave irradiation could be effective due to increased conductivity of the water (Hu et al., 2013). Perles et al. (2012) studied the effect of cation type and salinity on the stability of water/oil emulsions under the application of an electric field. The results indicated that the presence of salts increased the stability of the emulsion (Perles et al., 2012). Akbari & Biria. (2018) studied the effect of biodemulsifiers and the influence of salinity on its effect on breaking W/O emulsions. The results indicated that adding NaCl had a positive effect on the demulsification (Akbari & Biria, 2018).

2.6.2.4 Effect of water and oil content

The water and oil volume ratio is another parameter affecting the demulsification process (Dhandhi et al., 2021; Saad et al., 2020). Increasing the amount of water in the emulsion with the presence of the surfactant can ease the separation process. It is stated that higher water content promotes demulsification efficiency while decreasing the demulsifier dosage and time needed for the separation to occur, on the condition that the water content is in the range of 30 – 70% (volumetric fractions) (Yonguep et al., 2022). Z. Wang et al. (2018) studied the effect of ultrasonic crude oil demulsification and dehydration and the influence of water content on

the separation efficiency. The results showed that the water ratio had a complex influence on the dehydration rate as the dehydration rate decreased with the increase of water ratio up to 70 % and increased with the increase of water ratio above 70 % (Z. Wang et al., 2018).

2.6.2.5 Effect of emulsifier/demulsifier dosage

The characteristics of crude oil emulsions vary greatly. Consequently, chemical demulsifiers behave differently depending on the nature of the emulsion encountered (Yonguep et al., 2022). The demulsification process is influenced by the demulsifier dosage and the stability of the emulsion. An emulsion with a higher emulsifier ratio requires a significantly higher dosage of demulsifier (Saad et al., 2020). A low dosage of demulsifier may not lead to a total destabilization of the emulsion and not a complete separation. However, overdosing of the demulsifier may increase the stability of the emulsion. L. Zhang et al. (2018) investigated the ratio of oil separation of O/W emulsions and the effect of three types of surfactants in the concentrations range of 10 – 40 mgL⁻¹. The separation efficiency was different between the samples according to concentration and type of surfactant used. However, higher concentration led to a higher oil removal ratio (L. Zhang et al., 2018). Another study by Rajak et al. (2016) investigated the separation of oil from O/W emulsions and the effect of demulsifier dosage in the range of 10 – 100 mgL⁻¹. The results showed increased demulsification efficiency with increased demulsifier dosage due to the neutralization of emulsifiers (Rajak et al., 2016).

2.6.2.6 Effect of retention or settling time

In the context of demulsification, retention time is the time the emulsion stays in a non-agitated state to allow it to separate into its individual phases (Yonguep et al., 2022). A higher retention time enhances the gravity settling and demulsification efficiency due to enhanced demulsifier diffusion through the interface (Yonguep et al., 2022). Rajak et al. (2016) studied the separation of oil from O/W emulsions and investigated the effect of settling time on the demulsification efficiency. The results showed that the demulsification efficiency increased with increasing settling time but remained constant after 60 minutes. Further increase in the settling time would not increase the demulsification efficiency as the dynamic equilibrium of molecular motion at the oil-water interface was reached after 60 minutes (Rajak et al., 2016). It should, however, be noted that high retention time could lead to a re-emulsification and reduce the demulsification efficiency (Yonguep et al., 2022).

2.6.2.7 Effect of emulsion aging

The effect of emulsion aging or storage time prior to treatment could affect the demulsification efficiency as the emulsion properties tend to change after being stored for an extended period (Yonguep et al., 2022). Pajouhandeh et al. (2016) studied the influence of aging time on the phase separation of W/O emulsions. The results showed that the droplet size of the emulsion became significantly smaller after being stored for a long time (Pajouhandeh et al., 2016). During the study, a comparison of the fresh and the aged emulsion illustrated that the droplet diameter, droplet size distribution, and stability of the emulsion were time-dependent (Pajouhandeh et al., 2016). Emulsion properties (such as viscosity, droplet size distribution, interfacial films, and stability) tend to undergo some changes after being untreated for a prolonged time (Yonguep et al., 2022). These changes can negatively affect the demulsifiers and demulsification efficiency.

2.7 Environmental impact

Oil sludge enters the environment as a result of human activities. This includes deliberate dumping, improper treatment and management, storage, transportation, and landfill disposal (Ubani et al., 2013). This is of increasing concern because toxic substances in the sludge pose severe threats to the receiving environment (da Silva et al., 2012; Hu et al., 2013; Johnson & Affam, 2019).

By entering the terrestrial environment, oily sludge can significantly modify the surrounding soil's physical and chemical properties, resulting in morphological change (Hu et al., 2013; Johnson & Affam, 2019). Oil sludge-contaminated soil may create nutrient deficiency and stunted growth or demises in the vegetation of the receiving soil (Hu et al., 2013; Johnson & Affam, 2019). The high viscosity of the sludge causes its components to be fixed in the soil pores or form a continuous layer on the soil surface (Hu et al., 2013). Reduction in hygroscopic moisture, hydraulic conductivity, and water retention capacity of the soil is a consequence of this (Hu et al., 2013; Johnson & Affam, 2019). Components in the sludge with higher molecular weight could remain close to the soil surface and have been observed to form hydrophobic crusts that reduce water availability and water/air exchange (Robertson et al., 2007). Many PHC-contaminated soils will eventually take up water. However, its long-term effect has been documented on agricultural soils in western Canada (Robertson et al., 2007).

Contamination of this kind to the environment could lead to various toxic effects, which are caused by PHCs and heavy metals. A large amount of the heavy metals in the sludge have a cumulative effect and are of particular concern (Hu et al., 2013). The sludge composition includes high concentrations of PHCs and PAHs. The PAHs are of significant concern as they are genotoxic to humans and other ecological receptors (Ubani et al., 2013; H. Wang et al., 2018). The PHCs in the sludge may migrate through the soil profile and enter groundwater, which might be linked with other aquatic systems. This has a high potential for causing adverse consequences affecting the aquatic ecosystem (Wake, 2005).

Traditionally, the management of oil sludge was poorly performed by dumping it into dykes, ditches, trenches, or casks for subsequent burial without prior preparation of the area. The accumulation of sludge resulted in contamination of local water bodies, which caused the demise of aquatic species, persistent heavy metal contamination, and damage to the environmental areas (da Silva et al., 2012). If the sludge were disposed of in lagoons lined with cement and bricks, problems of odor and fire hazards would still be present (Hu et al., 2013). Oil sludge depositions in lagoons or landfills have also been characterized as a stationary source of atmospheric volatile organic compounds (VOCs) pollution (Hu et al., 2013; Ubani et al., 2013). Such atmospheric pollution can create health risks to the surrounding environment and communities (Hu et al., 2013).

Because of the hazardous nature of oil sludge, many countries have identified it as hazardous waste solids (Hui et al., 2020). Therefore, many regulations, such as the USA's Resource Conservation and Recovery Act (RCRA), have established strict standards for its handling, storage, and disposal (US EPA, 2015). Researchers have developed treatment technologies to adapt to stricter environmental regulations caused by traditionally oil sludge disposal methods (Hu et al., 2013; Hui et al., 2020). Oil sludge contains large amounts of crude oil, water, metal, and other recyclable resources composed of petroleum hydrocarbons. Therefore, it is considered a renewable energy source with a high potential value (Hui et al., 2020). Due to the continuous updating of environmental, sustainability, and other eco-environmental development and regulations, recycling is the optimal environmental solution for the disposal and treatment of this waste (Hui et al., 2020). The resource utilization of the sludge could effectively reduce the disposal volume and the degree of pollution of hazardous waste solids (Hui et al., 2020). In addition, it could also reduce the use of nonrenewable resources.

3. Laboratory project

This chapter describes the laboratory tests conducted for this thesis.

3.1 Basis for the laboratory testing

The laboratory work done in this thesis aimed to destabilize and separate oil sludges by utilizing environmentally friendly chemicals, thermal heating, and mechanical equipment. Chemicals and heat energy are used to destabilize the sludge, and centrifuges are used to enhance the settling and separation efficiency. Factors such as temperature, chemical dosage, and pH were to be tested. The applied gravitational force by centrifuges was fixed to better understand the influence of the experimental factors. The laboratory testing was performed in two steps: pre-screening and the main experiment. Centrifugal operation parameters were fixed to 2500 RCF¹ (relative centrifugal force) with a retention time of 4 minutes during the project.

3.1.1 Pre-screening

A pre-screening of different chemicals and pH was tested on the oil sludge to evaluate the destabilization effect. Pre-screening was done to specify and find optimal conditions for further testing. The findings found during pre-screening were used further in the main experiment. During pre-screening the temperature was fixed at a moderate temperature of 60 °C.

3.1.2 Main experiment

The proposed values for the main experiment were chosen based on information about the sludge from the supplier², pre-screening of the sludge, previous studies of Mudsplit chemicals³ and literature studies (Chapter 2). The temperature for most samples was fixed at 60 °C.

¹ RCF is expressed as units of gravity, and is equivalent to g-force

² Information from IBKA regarding the sludge from Mongstad stated that they were able to separate the sludge by heating it to 70 °C before centrifugation.

³ Previous studies on Mudsplit chemicals were done on oil-based mud

3.2 Methodology for Main experiment

The test conditions during the main experiment have been divided into two parts based on the sludge tested during the laboratory work. Centrifugal operation parameters were fixed to 2500 RCF with a retention time of 4 minutes.

3.2.1 Methodology for Mongstad oil sludge

Table 2 and Table 3 show test conditions conducted during the main experiment, which results from the pre-screening of the sludge. The table was inspired by Taguchi Design of Experiment software from Minitab. Each condition was repeated in two parallels to verify the method's validity. The chemicals tested for this sludge were Mudsplit1 and Mudsplit2 in combination with N-Sep. The Mudsplit chemicals used were diluted in a ratio of 1:10, as described in Appendix 1.

Table 2 Experimental conditions for Mudsplit1 & N-Sep and Mongstad oil sludge.

Sample	Temperature (°C)	Dosage MudSplit1 (vol/vol%)	Dosage N-Sep (vol/vol%)	pH
1	60	0.25	2	3.5
2	60	0.5	4	3.5
3	60	0.75	6	Neutral
4	60	1	8	Neutral
5	70	0.25	4	Neutral
6	70	0.5	2	Neutral
7	70	0.75	8	3.5
8	70	1	6	3.5
9	80	0.25	6	3.5
10	80	0.5	8	3.5
11	80	0.75	2	Neutral
12	80	1	4	Neutral
13	90	0.25	8	Neutral
14	90	0.5	6	Neutral
15	90	0.75	4	3.5
16	90	1	2	3.5

Table 3 Experimental conditions for Mudsplit1, Mudsplit2 and Mongstad sludge with fixed dosage of N-Sep (2 vol/vol %) and temperature of 60 °C.

Sample	Dosage (vol/vol%)	pH
1	0.05	Neutral
2	0.1	Neutral
3	0.15	Neutral
4	0.2	Neutral
5	0.05	3.5
6	0.1	3.5
7	0.15	3.5
8	0.2	3.5

3.2.2 Methodology for Brenda oil sludge

Table 4 and Table 5 show test conditions during the main experiment on Brenda sludge, which was performed using a trial-and-error approach. Each condition was repeated in two parallels. The chemicals tested for this sludge were Mudsplit1 and Mudsplit6. Mudsplit1 was diluted in a ratio of 1:10, according to Appendix 1. Mudsplit6 was not diluted as it was not soluble in water.

Table 4 Experimental conditions for Mudsplit1 and Brenda oil sludge with fixed temperature of 60 °C.

Sample	Dosage (vol/vol%)	pH
0	0	Neutral
1	0.05	Neutral
2	0.1	Neutral
3	0.15	Neutral
4	0.2	Neutral
5	0.25	Neutral
6	0.25	3.5
7	0.25	10

Table 5 Experimental conditions for Mudsplit6 and Brenda oil sludge with fixed temperature of 60 °C.

Sample	Dosage (vol/vol%)	pH
1	0.25	Neutral
2	0.5	Neutral
3	0.75	Neutral
4	1	Neutral

Experimental factors in Table 5 were tested with Mudsplit1 in situ by field engineers in Aberdeen and was therefore not tested in the laboratory.

3.3 Materials and equipment

Crude oil sludge from two different suppliers was tested in this work. Crude oil sludge was provided by IBKA and was collected from the crude oil storage tank at Equinor ASA refinery at Mongstad (presented in the thesis as Mongstad sludge). Equinor ASA provided a safety data sheet concerning the sludge, and some selected data is presented in Table 6 and Table 7. The second crude oil sludge was provided by Direct Waste Management LTD (presented in the thesis as Brenda sludge). Little information about this sludge is available; besides, it is an aged sludge that has been stored for about six years.

Table 6 Composition of constituents of the crude oil sludge provided by IBKA.

Compound	CAS number	EC-number	Concentration
Petroleum crude oil	8002-05-9	232-298-5	100 %
n-hexane	110-54-3	203-777-6	0.2 – 5 %
Total sulfur			0.50 – 2 %
Benzene	71-43-2	200-753-7	0.06 – 1.5 %

Table 7 Physical and chemical properties of the crude oil sludge provided by IBKA.

Parameter	Value/unit
pH	No data
Starting boiling point and boiling point range	< 35 °C
Flash point	< 23 °C
Relative density	0.8 – 0.9 g/cm ³
Viscosity	< 20.50 mm ² /s (at 40 °C)

Norwegian Technology AS provided the following chemicals used for destabilization of the sludge: MudSplit1, MudSplit2, MudSplit6 and N-Sep. The chemistry of these chemicals is confidential, and no detailed information will be available throughout the thesis.

Equipment used during the experiment were:

- Thermo Scientific Megafuge 16 Centrifuge (Fiberlite F15-6 x 100y Fixed Angle Rotor, radius 2.5 cm, Germany)
- Hettich Rotofix 46 Benchtop Centrifuge (rotor number 5694, rotor radius 173 mm, Germany)
- Retort apparatus (OFITE 50-mL Retort Kit, Houston, Texas, USA).

Other equipment used during the experiment:

- centrifuge tubes (15 mL) and bottles (250 mL)
- glass beakers (1000 mL, 500 mL, 400 mL, 50 mL)
- pipette
- syringes (10 mL)
- graduated cylinder (50 mL and 10 mL)
- Heidolph magnetic stirrer with heating function (Hei, Standard, Germany)
- Mettler Toledo pH-meter (Seven2Go S2, China) equipped with DJ113 electrode
- KERN precision weight (PLJ 600-2GM, Germany)
- laboratory thermometer

For systemizing the main experimental part, samples were marked according to; Mudsplit number, experimental condition and parallel. Figure 14 shows an example of how the samples were marked. The figure shows untreated (left) and treated (right) oil sludge. The treated sample is marked “1.10.2”, indicating that it was treated with Mudsplit1, and the sample was prepared according to conditions described in Table 2, as sample 10. The last number describes that this sample is parallel number two.

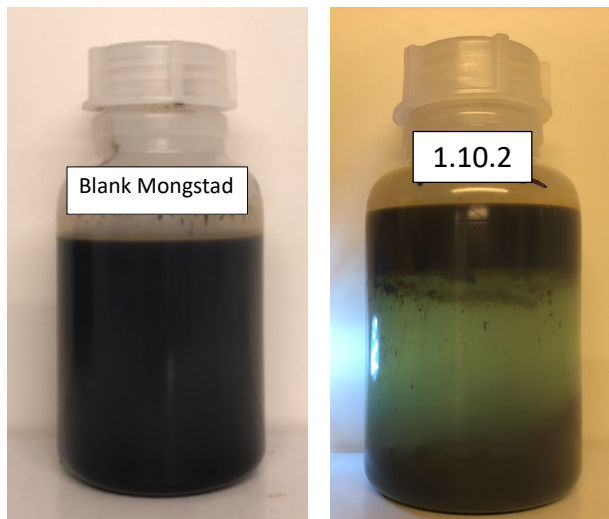
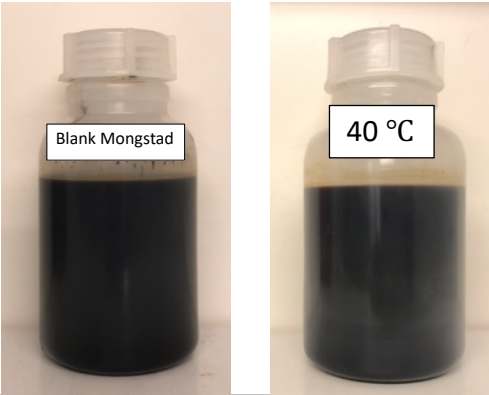
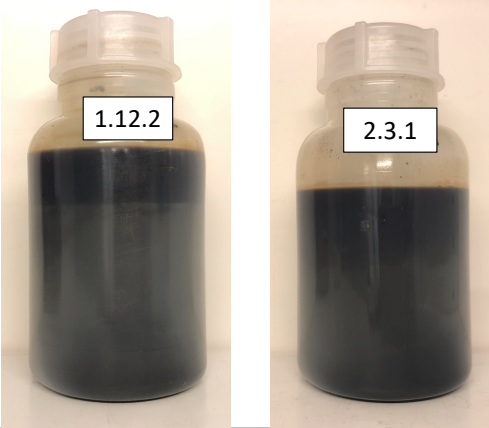
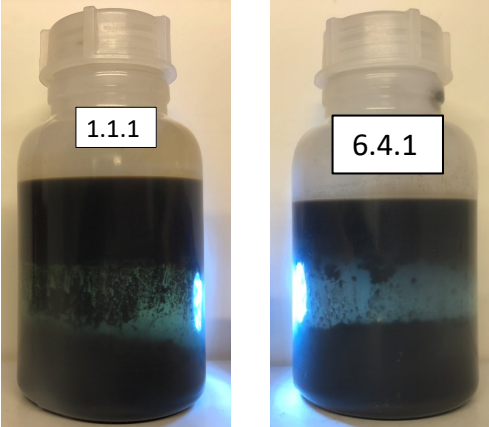
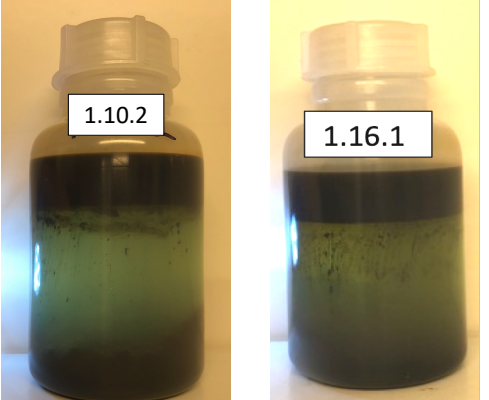


Figure 14 Difference between untreated (left) and treated (right) Mongstad oil sludge sample.

After treatment⁴ of the sludge, each sample was evaluated by observing the visual degree of phase separation. Samples were evaluated on a scale from 1 to 4 based on visual separation, according to Table 8.

⁴ Treatment includes chemical, thermal and mechanical treatment.

Table 8 Visual scale evaluation of three-phase separation ranging from 1 (worst) to 4 (best)

Grade/description	Visual example of samples separation	
<p>1 No change and/or slightly visible change, with visible upper phase.</p>		
<p>2 Separation without clearly defined three phases. Visible upper phase, indicating high concentration of oil. Middle phase is turbid and not clearly separated. Bottom phase is slightly visible. May be difficult to distinguish between the three phases.</p>		
<p>3 Three-phase separation, with defined phases. Defined upper phase. Middle phase is transparent and consist of small flocks. Defined bottom phase.</p>		
<p>4 Perfect three-phase separation with defined phases. Middle phase is transparent and, in most cases, free of flocks.</p>		

Before being treated, the sludge was quantified by measuring its volume fraction of oil, water, and solids. Determination of these fractions in the sludge was done by Retort analysis and is presented in the result section *4.1 Pre-screening*. The retort apparatus and the captured liquid fraction after the analysis are presented in Figure 15. After the sludge was treated, the upper phase was extracted from the sample and analyzed in the retort.



Figure 15 OFITE 50 mL Retort apparatus (left) and the captured liquid fraction after retort analysis (right)

The retort provides a method for separating and measuring the volumes of water, oil and solids contained in a sample. In the method, a known sample volume is heated (to 480 °C) in a retort chamber to vaporize the liquid components. The vapor is then condensed and collected in a graduated liquid receiver. The liquid volumes are determined by reading the oil and water phases on the graduated receiver, and Equations 9 and 10 are used to calculate the volume percentage of these components (OFITE, 2015). The total volume of solids (suspended solids and dissolved materials) is determined by subtracting the total final liquid volume collected from the total sample volume. The volume percentage of solids is then calculated using Equation 11.

$$\text{Volume percent (\% oil)} = V_O = \frac{100 (\text{Oil volume collected, mL})}{\text{Sample volume, mL}} \quad \text{Equation 9}$$

$$\text{Volume percent (\% water)} = V_W = \frac{100 (\text{Water volume collected, mL})}{\text{Sample volume, mL}} \quad \text{Equation 10}$$

$$\text{Volume percent (\% solids)} = V_S = 100 - (V_O + V_W) \quad \text{Equation 11}$$

The oil/water ratio (OWR) was calculated using Equations 12-14. OWR gives the ratio of percentage oil in the liquid phase and the percentage water in the liquid phase and thus indicates how much oil and water the sample contains. A high OWR value indicates high oil volume and low water volume, while a low OWR value indicates low oil volume and high water volume.

$$\text{OWR} = \frac{X}{Y} \quad \text{Equation 12}$$

$$X = \% \text{ oil in liquid phase} = \frac{(\text{volume percent oil} * 100)}{(\text{volume percent oil} + \text{volume percent water})} \quad \text{Equation 13}$$

$$Y = \% \text{ water in liquid phase} = \frac{(\text{volume percent water} * 100)}{(\text{volume percent oil} + \text{volume percent water})} \quad \text{Equation 14}$$

OWR was used as an additional factor to give an indication of how effective the destabilization process was in the experiment. OWR was used in the investigated samples, where the upper phase contained oil and water. In addition, some selected bottom phases underwent retort analysis to determine how much oil and water it contained. Figure 16 illustrates the expected three-phase separation process of the sludge.

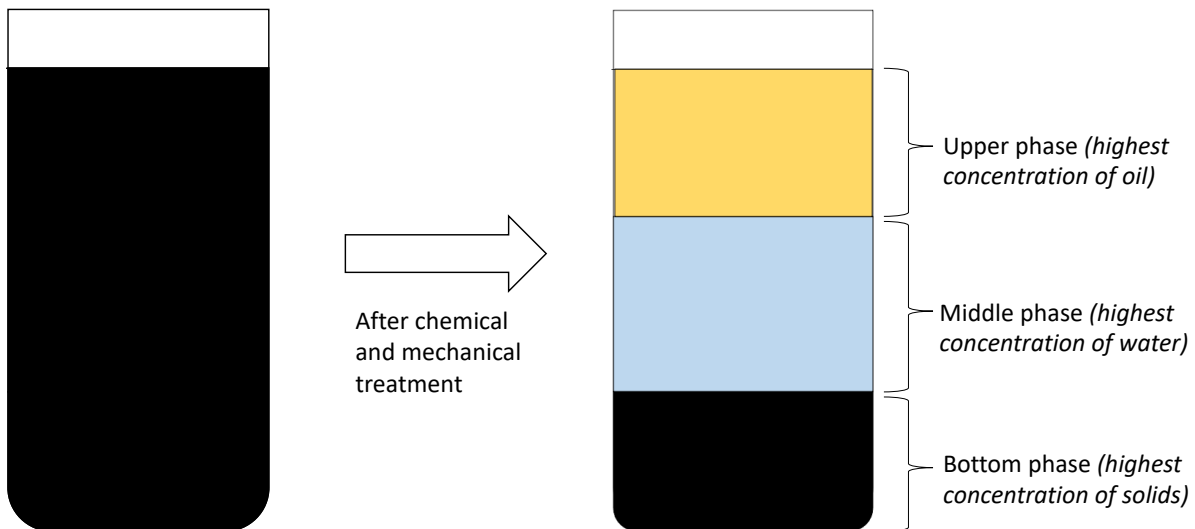


Figure 16 Untreated sample (left) and treated sample (right) with three phase separation. Upper phase on top, middle phase in the middle, and bottom phase at the bottom. The upper phase (50 mL) was analyzed by retort apparatus to determine its content of oil, water, and solids. Some selected bottom phases were also analyzed by retort apparatus.

3.4 Experimental procedure

The laboratory testing was done to separate the sludge into three phases. The testing was done according to the procedure described below. Time constrictions made pre-screening of Brenda sludge insufficient.

The N-Sep solution was prepared according to the description in Appendix 1.

Effect of chemical dosing

- a) Observation of changes in viscosity in the sludge samples after addition of Mudsplit chemicals and N-Sep.

3.4.1 Pre-screening Mongstad oil sludge

Effect of MudSplit1 and MudSplit2

The effect of chemical dosing was performed on Mongstad sludge with MudSplit1 and MudSplit2 in the concentration range; 0.05 %, 0.25 %, 0.5 %, 0.75 % and 1 %.

1. The beaker glass (400 mL) containing a crude oil sludge sample of 200 mL was heated by using a magnetic stirrer with heating function to 60 °C.
2. A beaker glass (50 mL) was filled with 40 mL of the sample.
3. Appropriate amount of MudSplit was added and mixed for 1 minute.
4. The sample was poured into a centrifuge tube (15 mL).
5. Mechanical centrifugation by Thermo Scientific Megafuge 16 centrifuge with fixed RCF was conducted immediately.
6. Visual evaluation of phase separation

Effect of the combination of Mudsplit1 and N-Sep in *Mongstad sludge*

The procedure described below was performed four times with an increased dosage of N-Sep (*step 2*), in the following concentrations (vol/vol %): 2, 4, 6 and 8.

1. The beaker glass (400 mL) containing a crude oil sludge samples of 200 mL was heated by using a magnetic stirrer with heating function to 60 °C.
2. Appropriate amount of N-Sep was added to the solution and mixed.
3. Six beaker glass (50 mL) was filled with 20 mL of the solution from step 2.

4. Appropriate amounts of Mudsplit1 were added to the beaker glass from step 3 in the following concentrations (vol/vol %): 0.25, 0.5, 0.75, 1, 2 and 4.
5. The samples were poured into centrifuge tubes (15 mL).
6. Mechanical centrifugation by Thermo Scientific Megafuge 16 centrifuge with fixed RCF was conducted immediately.
7. Visual evaluation of phase separation and grading was done immediately.

Effect of pH

1. Beaker glass containing crude oil sludge samples (200 mL) was heated to 60 °C using a magnetic stirrer with a heating function.
2. MudSplit chemicals were added 0.25 vol/vol %.
3. The pH was adjusted to 3.5 and 10 by the addition of 25⁵ drops HCl (30 %) and 25 drops NaOH (25 %), respectively.
4. The solution was poured into centrifuge tubes (15 mL).
5. Mechanical centrifugation by Thermo Scientific Megafuge 16 centrifuge with fixed RCF.
6. Visual evaluation of phase separation and grading.



Figure 17 Crude oil sludge sample (Mongstad oil sludge)

⁵ 1 drop is equivalent to approximately 0.05 mL. The stated drops for HCl and NaOH are an approximation and range from 20 to 25.

3.4.2 Main experiment

The main experiment was performed as described below. A simplified illustration of the procedure is shown in Figure 18.

1. The beaker glass (400 mL) containing 200 mL of oil sludge was heated by using a magnetic stirrer with heating function to the proper temperature according to the tables presented in chapter 3.2 *Methodology*. The temperature was measured using a laboratory thermometer.
2. Appropriate amounts of chemicals were added according to the tables in chapter 3.2 *Methodology*. The sample was mixed for 1 minute.
3. According to the tables presented in chapter 3.2 *Methodology*, if the pH was listed as other than “Neutral”, the pH was adjusted by addition of HCl (30 %) or NaOH (25 %). The pH was measured with a pH meter.
4. The sample was poured into a centrifuge bottle.
5. Mechanical centrifugation by Hettich Rotofix 46 centrifuge was conducted immediately.
6. Visual evaluation of phase separation and grading was done immediately.
7. The sample was let to settle overnight before the upper phase was analyzed by the retort apparatus described under the heading *Retort analysis*.

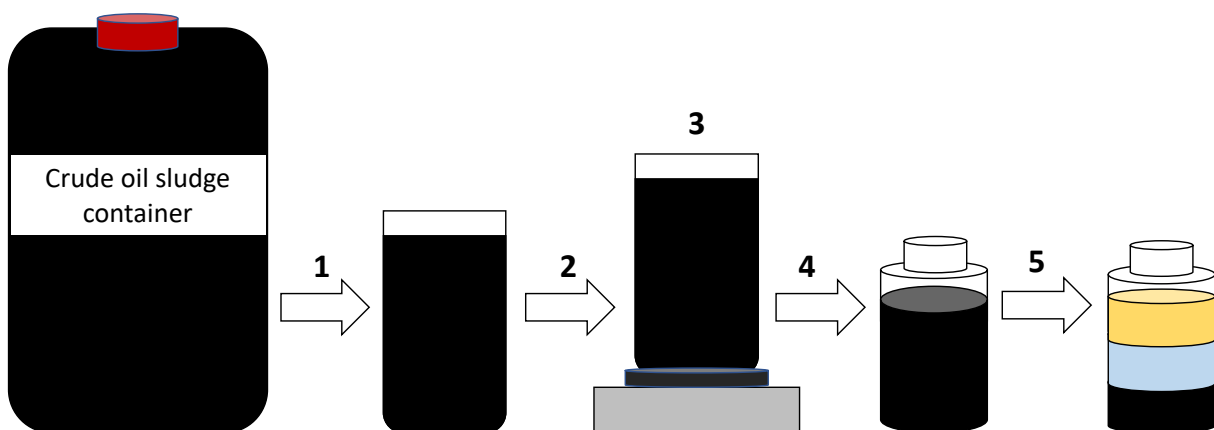


Figure 18 Simplified illustration of experimental procedure: (1) 200 mL sludge sample is collected from the sludge container, (2) the sample is heated using a magnetic stirrer with heating function, (3) chemicals are added, (4) the sample is poured into a centrifuge bottle and (5) the sample is centrifuged and separated. The upper phase is analyzed further by retort apparatus to determine the quality of the oil.

Effect of temperature on the destabilization effect in *Mongstad oil sludge*

1. A beaker glass (400 mL) containing crude oil sludge samples of 200 mL was heated using a magnetic stirrer with heating function to 20 °C, 40 °C and 60 °C, respectively.
2. The samples were poured into centrifuge bottles.
3. Mechanical centrifugation by Hettich Rotofix 46 centrifuge was conducted immediately.
4. Visual evaluation of phase separation.
5. The upper phase was extracted from the sample and analyzed by retort apparatus as described below.

Retort analysis

After a successful three-phase separation, the retort apparatus was used to analyze the upper phase. The upper phase from two parallel samples was extracted using a 10 mL syringe and analyzed in the retort. Additionally, some selected bottom phases were analyzed. The bottom phases from two parallel samples were mixed and analyzed in the retort. The procedure for the retort analyses is described below.

Retort analysis were performed as follow:

1. A pipe cleaner was used to clear the spout, leading to the condenser, of any obstructions.
2. Steel wool was packed into the expansion chamber.
3. The retort cup was filled slowly with the upper phase (or bottom phase) resulting from the main experiment.
4. The lid was placed onto the cup in a way that some excess fluid extruded from the hole in the lid to ensure a total sample volume of 50 mL
5. The threads on the retort cup were lubricated with thread lubricant.
6. The retort cup was placed onto the expansion chamber, and carefully hand tightened.
7. The expansion chamber tube was inserted into the Ultra-Torr connection on the condenser, and the screw on the connector was tightened.
8. The retort chamber was placed into the heater block, and the insulating lid was closed.
9. A graduated cylinder was used as the liquid receiver and was placed under the condenser discharge tube.
10. The analysis was conducted at 480 °C, and the sample was continuously heated for at least ten minutes beyond the time no more condensate was being collected.

11. The graduated cylinder was removed and allowed to cool before the collected volume of water and oil was recorded.
12. The retort chamber and condenser were removed to allow it to air cool before the retort cup was measured to record the mass of solids in the sample.
13. The measured volume of water and oil was converted into volume percentage (Equations 9 and 10), and the oil/water ratio was calculated by Equations 12-14.
14. The retort chamber was cleaned and prepared for the next sample.

Flame test

A flame test was used to examine the upper phases that were expected to contain a significant amount of water. The procedure of the flame test is described below. If the upper phase burned immediately after being exposed to flames, the oil content was high, and the water content was low. However, if it struggled to create a flame, or if the flame cracked, water content was significant.

The flame test was performed as follows:

1. A small amount of the upper phase was taken out of the sample and set on fire in a controlled manner.
2. Observation of the flame and how the fluid burned.

4. Results

This section presents the main results of the experimental research. The section is divided into two parts: pre-screening and the main experiment. All the results in the form of raw data and tables are attached in Appendixes 5 to 8.

4.1 Pre-screening

Pre-screening was performed to gather information about the sludge and its reaction to different chemicals. The information found in the pre-screening was optimized and used further in the main experiment.

The results include quantification of untreated⁶ sludge, which is quantified by retort analysis to determine the sludge's volume percentage of oil, water, and solids. The results describe the sludge's reaction to the applied chemicals and its visual separation efficiency after chemical, thermal and mechanical treatment.

4.1.1 Pre-screening Mongstad sludge

Untreated oil sludge from Mongstad was quantified by a retort analysis to determine its content of oil, water, and solids. The results are presented in Table 9. The pH of the sludge solution was measured to 7.1 at 60 °C and is hereafter referred to as this sludge's "natural" pH.

Table 9 Results from retort analysis for blank sample Mongstad sludge

Volume % Oil	28
Volume % Water	60
Volume % Solids	12
OWR	0.5

⁶Untreated sludge (blank sample) refers to raw sludge, which is neither chemical, thermal nor, mechanically treated.

Pre-screening with Mudsplit1, Mudsplit2 and N-Sep

Heating the sludge to 60 °C resulted in a visible decrease in viscosity. After adding of MudSplit1 to the sludge, a visible additional decrease in viscosity was obtained while moderate mixing. Samples containing a MudSplit1 concentration ranging from 0.05 % to 1 % were heated to 60 °C and centrifuged to observe the separation effect. Visual separation was moderate, and most samples included a visible upper- and middle phase. Results in pictures of the samples are presented in Appendix 5.

Viscosity reduction was visibly obtained by the addition of MudSpli2 to the sludge. Samples containing MudSplit2 (concentration ranging from 0.05 % to 1 %) were heated to 60 °C and centrifuged, and the separation efficiency was observed. Visible separation efficiency was poor, with no or slightly visible effect. Results in pictures of the samples are presented in Appendix 5.

The addition of N-Sep to the sludge showed a visible increase in the viscosity at first. After some mixing, the viscosity decreased.

Pre-screening with Mudsplit1 in combination with N-Sep

The addition of Mudsplit1 in combination with N-Sep gave better visual separation efficiency after heating to 60 °C and centrifugation. Testing was done in various combinations and is presented in Table 10. The treated samples are evaluated on a scale from 1 (worst) to 5 (best) based on visual separation according to the scale in Appendix 4.

Table 10 Effect of Mudsplit1 combined with N-Sep at various concentrations for destabilization of Mongstad sludge. Results include corresponding visual separation grades based on the scale in Appendix 4. The temperature was fixed at 60 °C.

Sample	Dosage N-Sep (vol/vol %)	Dosage Mudsplit1 (vol/vol %)	Visual separation grade scale
1	2	0.25	1
2		0.5	1
3		0.75	2
4		1	2
5		2	3
6		4	4
7	4	0.25	2
8		0.5	2
9		0.75	3
10		1	3
11		2	4
12		4	4
13	6	0.25	3
14		0.5	3
15		0.75	4
16		1	3
17		2	4
18		4	4
19	8	0.25	3
20		0.5	3
21		0.75	3
22		1	4
23		2	4
24		4	5

The results in Table 10 show that at high dosages of both Mudsplit1 and N-Sep, successful three-phase separation with defined phases was achieved. For the main experiment, dosages of Mudsplit above 1 % were not performed.

Effect of pH

The effect of acidic and alkaline chemical environments was tested. Samples was heated to 60 °C, followed by addition of MudSplit1 and NaOH and HCl, before centrifugation. Visual separation efficiency improved in an acidic environment and was not significantly improved in an alkaline environment. Pictures of the samples are presented in Figure 19.



Figure 19 Effect of alkaline (left) and acidic (right) chemical environment on Mongstad sludge

At pH 3.5, the middle phase became less contaminated and became transparent, which is not perfectly illustrated in Figure 19.

4.1.2 Pre-screening Brenda sludge

Untreated oil sludge from Brenda was quantified to determine its oil, water, and solids content. The results are presented in Table 11. The pH of the sludge solution was measured to 6.0 at 60 °C and is hereafter referred to as this sludge’s “natural” pH.

Table 11 Results from retort analysis for blank sample Brenda sludge

Volume % Oil	40
Volume % Water	48
Volume % Solids	12
OWR	1

A thorough pre-screening of Brenda sludge was not possible due to limited time. The author of this thesis did not perform the screening of the sludge’s reaction to MudSplit1, and results in the form of pictures are omitted.

Pre-screening with Mudspl1 and N-Sep

Pre-screening of the sludge showed a positive reaction with MudSplit1. A visible decrease in viscosity was obtained. With a dosage of 0.02 vol/vol % and a temperature of 60 °C, visible three-phase separation with clearly separated phases was achieved. The addition of N-Sep gave no additional visible effect and was not tested further in the main experiment.

4.3 Main experiment Mongstad sludge

Crude oil sludge received from the oil storage tank at Mongstad was tested with Mudsplit1 and Mudsplit2 in combination with the polymer N-Sep. The combination of Mudsplit and N-Sep is thought to promote destabilization and was a request from the supplier.

The results include a description of the visual separation efficiency of the samples (according to Table 8) after chemical, thermal and mechanical treatment. The results also include an analysis of the upper phase of the samples, which is analyzed by retort apparatus. In addition, the bottom phases of selected samples are analyzed by retort apparatus and are presented in the results. In the following tables, * indicates no OWR value as the liquid phase consisted of 100 % oil relative to water.

4.3.1 Mongstad sludge and Mudsplit1



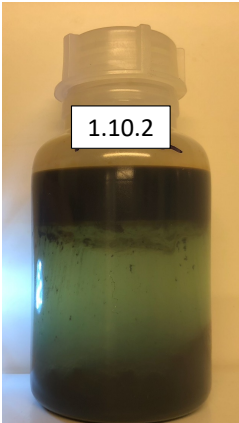
The sludge was tested with Mudsplit1 in combination with N-Sep, according to Table 2. The following results presented in Table 12 were obtained during the experiment.

Table 12 Results of retort analysis of the upper phases after treatment of Mongstad sludge by MudSplit1 according to Table 2. The results include volume percentages of oil, water, and solids. The treated samples were graded based on visual separation efficiency according to the scale in Table 8.

Sample	Visual separation grade scale	Volume % oil	Volume % water	Volume % solids	OWR
1.1.1 and 1.1.2	3	94	0	6	*
1.2.1 and 1.2.2	3	94	0	6	*
1.3.1 and 1.3.2	2	95	0	5	*
1.4.1 and 1.4.2	2	92	0	8	*
1.5.1 and 1.5.2	2	93	0	7	*
1.6.1 and 1.6.2	2	92	0	8	*
1.7.1 and 1.7.2	4	90	2	8	45
1.8.1 and 1.8.2	4	92	0	8	*
1.9.1 and 1.9.2	4	91	0	9	*
1.10.1 and 1.10.2	4	90	0	10	*
1.11.1 and 1.11.2	2	92	0	8	*
1.12.1 and 1.12.2	2	90	0	10	*
1.13.1 and 1.13.2	2	94	0	6	*
1.14.1 and 1.14.2	2	90	4	6	22.5
1.15.1 and 1.15.2	4	95	0	5	*
1.16.1 and 1.16.2	4	96	0	4	*

Table 13 presents three performed experiments based on visual separation degree according to visual scale in Table 8. Samples in Table 13 are set up from the lowest separation efficiency achieved (graded 2) to the highest separation (graded 4).

Table 13 Visual evaluation of destabilization of Mongstad sludge by Mudsplit1 and N-Sep in various conditions

Sample	Visual separation grade	Experimental condition	Description of destabilization effect
	2	80 °C 1 % Mudsplit1 4 % N-Sep Neutral pH	Dark upper phase on top of the sample. Middle phase is turbid and contaminated with hydrocarbons. Bottom phase is slightly visible.
	3	60 °C 0.25 % Mudsplit1 2 % N-Sep pH 3.5	Dark upper phase on top of the sample. Middle phase is transparent and contaminated with flocks. Dense bottom phase at the bottom.
	4	80 °C 0.5 % Mudsplit1 8 % N-Sep pH 3.5	Defined upper phase on top of the sample. Middle phase is clear and is not contaminated by flocks. Dense bottom phase at bottom of sample.

4.3.1.1 Optimization of Mudsplit1 dosage

As most of the samples in Table 12 included an upper phase of relatively high-quality oil, an optimization by the lowest possible dosage is presented in Table 14. The sludge was tested with Mudsplit1 in combination with a fixed N-Sep dosage of 2 % (vol/vol %). The experimental factors followed those described in Table 3.

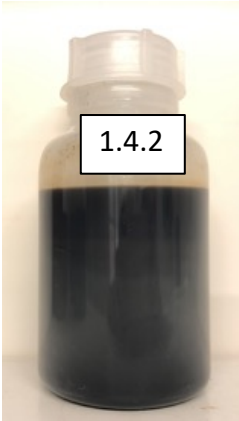
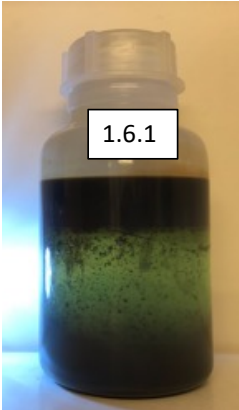
Table 14 Results of retort analysis of the upper phases after treatment of Mongstad sludge by MudSplit1 according to Table 3. The results include volume percentages of oil, water, and solids. The treated samples were graded based on visual separation efficiency according to Table 8.

Sample	Visual separation grade scale	Volume % oil	Volume % water	Volume solids	%	OWR
1.1.1 and 1.1.2	2	92	0	8		*
1.2.1 and 1.2.2	2	92	0	8		*
1.3.1 and 1.3.2	2	92	0	8		*
1.4.1 and 1.4.2	2	90	0	10		*
1.5.1 and 1.5.2	3	86	5	9		17.2
1.6.1 and 1.6.2	3	90	2	8		45
1.7.1 and 1.7.2	3	90	1	9		90
1.8.1 and 1.8.2	3	91	0	9		*

The result in Table 14 show increased volume percentage of solids in the upper phase at dosages between 0.05 and 0.2 %, compared to those in Table 12. The samples with a pH of 3.5, which had a chemical dosage below 0.2 % contained a small amount of water in the upper phase.

Table 15 presents two samples from the performed experiment. The only visual separation grade in this experiment was 2 and 3, according to Table 8.

Table 15 Visual evaluation of destabilization of Mongstad sludge by optimization of Mudsplit1 dosages

Sample	Visual separation grade	Experimental condition	Description of destabilization effect
	2	60 °C 0.2 % Mudsplit1 2 % N-Sep Neutral pH	Visible upper phase at top of the sample. Middle phase is turbid and contaminated with hydrocarbons. Slightly visible bottom phase.
	3	60 °C 0.1 % Mudsplit1 2 % N-Sep pH 3.5	Defined upper phase at top of the sample. Middle phase is transparent and contaminated by flocks. Dense bottom phase at bottom.

Some selected bottom phases were analyzed by retort apparatus and is presented in Table 16. It is apparent that the bottom phase is an emulsion with an unexpected low volume of solids.

Table 16 Results of retort analysis of selected bottom phases after treatment of Mongstad sludge with Mudsplit1, which include volume percentage of oil, water, and solids.

Sample	Volume % oil	Volume % water	Volume % solids	OWR
1.1.1 and 1.1.2	25	60	15	0.4
1.4.1 and 1.4.2	24	58	18	0.4
1.5.1 and 1.5.2	28	56	16	0.5
1.8.1 and 1.8.2	30	54	16	0.6

4.3.2 Mongstad sludge and Mudsplit2

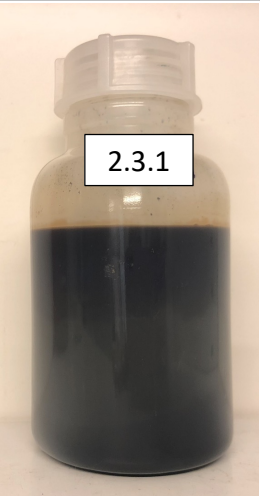
Mongstad sludge was tested with Mudsplit2 in combination with fixed N-Sep dosage of 2 % (vol/vol %). The experimental factors followed those described in Table 3. The results are presented in Table 17.

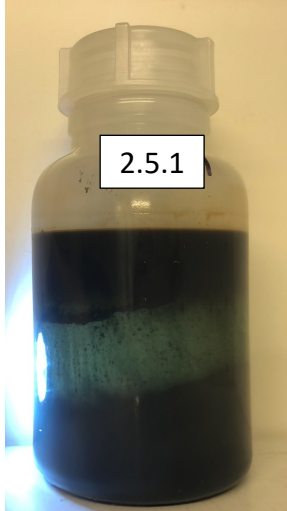
Table 17 Results of retort analysis of the upper phases after treatment of Mongstad sludge by MudSplit2 according to Table 3. The results include volume percentages of oil, water, and solids. The treated samples were graded based on visual separation efficiency according to Table 8.

Sample	Visual separation grade scale	Volume % oil	Volume % water	Volume % solids	OWR
2.1.1 and 2.1.2	2	88	0	12	*
2.2.1 and 2.2.2	2	90	0	10	*
2.3.1 and 2.3.2	2	92	0	8	*
2.4.1 and 2.4.2	2	92	0	8	*
2.5.1 and 2.5.2	3	90	0	10	*
2.6.1 and 2.6.2	3	90	0	10	*
2.7.1 and 2.7.2	3	90	0	10	*
2.8.1 and 2.8.2	3	92	0	8	*

Table 18 presents two samples in the performed experiment. Visual separation was graded as 2 and 3 in this experiment, according to Table 8.

Table 18 Visual evaluation of destabilization of Mongstad sludge by Mudsplit2

Sample	Visual separation grade	Experimental condition	Description of destabilization effect
	2	60 °C 0.15 % Mudsplit2 2 % N-Sep Neutral pH	Visible upper phase at top. Middle phase is turbid and contaminated with hydrocarbons. Slightly visible bottom phase.

	3	60 °C 0.05 % Mudsplit2 2 % N-Sep pH 3.5	Clear upper phase at top of the sample. Middle phase is transparent and contaminated by small flocks. Dense bottom phase at the bottom.
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Some selected bottom phases were analyzed by retort apparatus and is presented in Table 19. The results presented in Table 19 is similar to those presented in Table 16.

Table 19 Results of retort analysis of selected bottom phases after treatment of Mongstad sludge with Mudsplit2, which include volume percentage of oil, water, and solids.

Sample	Volume % oil	Volume % water	Volume % solids	OWR
2.1.1 and 2.1.2	24	60	16	0.4
2.4.1 and 2.4.2	24	62	14	0.4
2.5.1 and 2.5.2	26	58	16	0.4
2.8.1 and 2.8.2	30	56	14	0.5

4.3.3 Mongstad sludge and effect of thermal heating

Destabilizing the sludge was possible by thermal and mechanical treatment without the use of chemicals. By increasing the temperature, a slight reduction in viscosity was visibly obtained while moderate mixing. Visual separation efficiency was lower than those treated with chemicals; however, the analyzed upper phase was of high quality after centrifugation. The results are presented in Table 20.

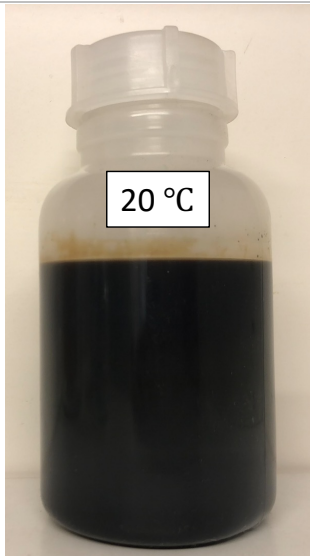
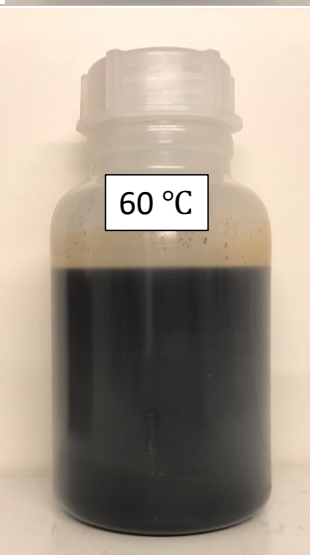
Table 20 Effect of thermal heating on the separation efficiency of Mongstad sludge. The result of the analyzed upper phase includes volume percentage of oil, water, and solids.

Sample	Visual separation grade scale	Volume % oil	Volume % water	Volume % solids
20 °C	1	88	2	10
40 °C	1	92	0	8
60 °C	2	92	0	8

The results in Table 20 indicate that increased temperature from 20 °C to 40 °C results in slightly better separation efficiency. Increasing the temperature further, from 40 °C to 60 °C, gave no increased separation efficiency.

Table 21 presents two samples which were evaluated as visual separation grade 1 and 2.

Table 21 Visual evaluation of destabilization of Mongstad sludge by thermal and mechanical treatment

Sample	Visual separation grade	Experimental condition	Description of destabilization effect
	1	20 °C Neutral pH	<p>Slightly visible upper phase.</p> <p>Middle phase and bottom phase are not visually separated.</p>
	2	60 °C Neutral pH	<p>Visible upper phase at top.</p> <p>Middle phase is turbid and contaminated.</p> <p>Slightly visible bottom phase.</p>

4.4 Main experiment Brenda sludge

Brenda oil sludge is an aged sludge that has been stored for a long time. The results include a description of the visual separation efficiency of the samples (according to Table 8) after chemical, thermal and mechanical treatment. The results also include an analysis of the upper phase of the samples, which is analyzed by retort apparatus.

Great visual separation was obtained after treatment. However, after a thorough examination, it was visible that the upper phase consisted of two phases. The less dense phase was analyzed and is presented in the results below. The denser phase was distinctly an emulsified phase with high concentrations of oil and water. This phase was tested by a flame test rather than a retort analysis.

The results of the analyzed upper phases in Table 22 and Table 24 are presented as mass percentages instead of volume percentages. This is due to the small volume of the upper phase after treatment. This made it impossible to get a fixed sample volume of 50 mL, for the retort analysis. The mass percentage is calculated according to the equations in Appendix 3.

4.4.1 Brenda sludge and Mudsplit1

Brenda sludge was tested with Mudsplit1 according to Table 4. Higher dosages (above 0.25 %) of Mudsplit1 was tested in situ by field engineers in Aberdeen and did not give increased separation efficiency. The laboratory results are presented in Table 22.

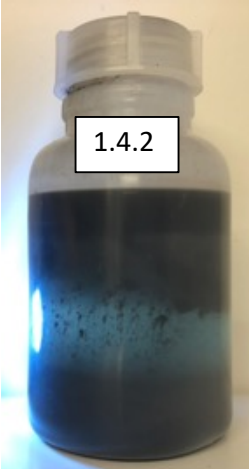
Table 22 Results of retort analysis of the upper phases after treatment of Brenda sludge by MudSplit1 according to Table 4. The results include mass percentages of oil, water, and solids. The treated samples were graded based on visual separation efficiency according to Table 8.

Sample	Visual separation grade scale	Mass % oil	Mass % water	Mass % solids
1.0.1 and 1.0.2	3	96.8	1.6	1.6
1.1.1 and 1.1.2	3	96.7	1.6	1.8
1.2.1 and 1.2.2	3	96.3	1.6	2.1
1.3.1 and 1.3.2	3	96.7	1.6	1.7
1.4.1 and 1.4.2	3	96.3	1.7	2.0
1.5.1 and 1.5.2	3	95.8	1.7	2.5
1.6.1 and 1.6.2	3	-	-	-
1.7.1 and 1.7.2	3	-	-	-

The visual separation degree was similar for all the samples in Table 22. It was not performed a retort analysis of samples 1.6.1/1.6.2 and 1.7.1/1.7.2 based on visual examination of the upper phase. A flame test was performed on these samples, indicating a high volume of oil and water, and consequently a poor-quality oil. The results in Table 22 show no increased separation efficiency by increased chemical dosage.

Table 23 presents one of the samples from the performed experiment. The visual separation grade was 3 and was graded according to Table 8.

Table 23 Visual evaluation of destabilization of Brenda sludge by Mudsplit1

Sample	Visual separation grade	Experimental condition	Description of destabilization effect
	3	60 °C 0.2 % Mudsplit1 Neutral pH	<p>Visual upper phases. The less dense phase on the top, and the denser emulsified phase underneath.</p> <p>Middle phase is transparent and contaminated by flocks.</p> <p>Dense bottom phase at the bottom.</p>

4.4.2 Brenda sludge and Mudsplit6

Brenda sludge was tested with Mudsplit6 according to Table 5. The results are presented in Table 24.

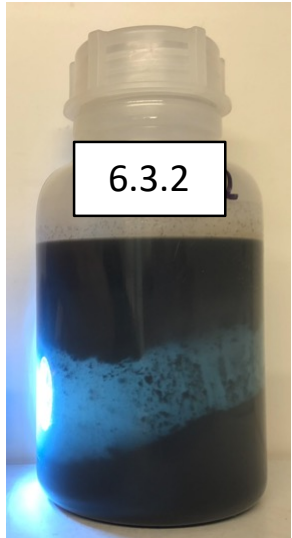
Table 24 Results of retort analysis of the upper phases after treatment of Brenda sludge by MudSplit6 according to Table 5. The results include mass percentages of oil, water, and solids. The treated samples were graded based on visual separation efficiency according to Table 8.

Sample	Visual separation grade scale	Mass % oil	Mass % water	Mass % solids
6.1.1 and 6.1.2	3	95.4	1.8	2.8
6.2.1 and 6.2.2	3	96.0	1.9	2.0
6.3.1 and 6.3.2	3	97.5	0.6	1.8
6.4.1 and 6.4.2	3	97.6	0.7	1.7

The samples in Table 24 had similar visual separation degrees. The table shows a trend with no significant increase in separation efficacy by increased dosage.

Table 25 presents one of the samples from the performed experiment. The visual separation grade was 3 and was graded according to Table 8.

Table 25 Visual evaluation of destabilization of Brenda sludge by Mudsplit6

Sample	Visual separation grade	Experimental condition	Description of destabilization effect
	3	<p>60 °C</p> <p>0.75 % Mudsplit6</p> <p>Neutral pH</p>	<p>Two upper phases. The less dense phase on the top, and denser emulsified phase underneath.</p> <p>Middle phase is transparent and contaminated by flocks.</p> <p>Dense bottom phase at bottom.</p>

5. Discussion

This chapter presents an analysis of the results obtained during the experimental testing. In this study, it is essential that the samples are representative so that each sample has the same composition. The sampling is, however, associated with uncertainties. The sludge tends to settle heavier fractions of its components (solids, water, etc.) after being stationary for a period. Therefore, the sludge container was mixed thoroughly before each sampling by manually shaking the container. When the container was full (or close to full), the mixing was less efficient due to limited free head space compared to when the container was half full. Insufficient mixing before sampling could be a source of error that could impact the results.

5.1 Pre-screening of Mongstad sludge

Untreated Mongstad sludge was quantified by retort analysis to determine its volume percentage of oil, water, and solids. The calculated OWR was 0.5, indicating that the sludge consists of a high volume of water. As water makes up most of the sludge's volume (60 %, Table 9), it could be suggested that this sludge is an O/W emulsion.

A visible reduction in the sludge's viscosity was observed by increasing its temperature. The addition of MudSplit1 and MudSplit2 gave a slightly additional reduction in viscosity. However, during pre-screening with MudSplit1 and MudSplit2, no perfect three-phase separation was obtained.

A successful three-phase separation was obtained by adding MudSplit1 in combination with N-Sep. The combination of N-Sep seemed to facilitate flocculation and ease the separation efficiency. High dosages of MudSplit (>1 %) and N-Sep gave positive visual three-phase separation. As the percentage of N-Sep increased, the amount of MudSplit1 needed to achieve an acceptable visual three-phase separation decreased (Table 10)

The effect of pH was investigated during pre-screening. The separation efficiency was significantly improved by decreasing the pH to 3.5. Decreasing the pH resulted in the middle phase becoming more transparent and less contaminated. This can be explained by the presence of NAs in the sludge and its acid-base equilibrium reaction. At neutral pH, the NAs will partition and dissociate into the aqueous phase, contaminating the aqueous phase with hydrocarbons. By lowering the pH to 3.5, the dissociated form will be protonated. Because the

undissociated form is more oil-soluble, it will move to the oil phase and make the aqueous phase transparent and less contaminated. At pH 10, no significant increase in separation efficiency was obtained, which could be due to that NAs are more soluble in the aqueous phase at elevated pH.

Pre-screening was performed with low sample volume to find optimal chemical dosages while limiting the use of sample volume. This approach proved to be insufficient, as the small volume led to misleading visual separation efficiency. It was hard to distinguish between poor and acceptable visual separation efficiency when the visual separation was graded between 1 and 3, according to the grade scale in Appendix 4. This approach also did not give any information on the quality of the upper phase.

5.2 Pre-screening of Brenda sludge

Brenda oil sludge was quantified by retort analysis, and the calculated OWR was 1. The OWR value indicates that the content of oil and water in the sludge was close to equal. The content of water was slightly higher than that of oil. Based on the quantification of the sludge's percentages of oil and water, it is not suitable to suggest what type of emulsion this is. The pH of the sludge was measured to 6.0, which is lower than typical oil sludges, which have pH values in the range of 6.5 – 7.5. The lower pH could be due to the long storage time of the sludge, which could lead to degradation of the sludge's components and changes in its properties.

Pre-screening of Brenda sludge with the addition of MudSplit1 gave a visual decrease in viscosity. When the sludge was heated to 60 °C in combination with low dosages of MudSplit1, successful three-phase separation was achieved after centrifugation. The addition of N-Sep with MudSplit1 gave no further visual increase in the separation efficiency. No further pre-screening was conducted for this sludge, and the methodology for further testing was performed as a trial-and-error approach.

5.3 Retort analysis and sources of error

After treatment and separation of the sludge samples, the upper phase was analyzed by retort analysis to determine the quality of the oil in the phase. Although retort analysis provides relatively high accuracy results, some sources of error are unavoidable.

An accurate analysis is dependent on the condenser in the retort apparatus. If the function of the condenser is impaired for some reason, it will affect the results negatively. During retort analysis, the analyzed sample is led through a condenser, and the condensate is collected in a graduated cylinder. The samples were continuously heated at 480 °C for at least ten minutes beyond the time no more condensate was being collected. However, how long the samples needed to be continuously heated after reaching 480 °C varied. This could account for sources of errors, such as uncertainties related to when all the condensate is collected. If the retort apparatus is turned off too early, the collected liquid would be of falsely low volume. The result of the sample's retort analysis would then get a lower volume percentage of condensate. The following sample would then get a falsely high percentage of condensate collected, as the condensate left in the condenser would be collected in this new sample. This source of error might account for the variability in the calculated volume percentage of oil, water, and solids.

5.4 Main experiment Mongstad sludge

5.4.1 Mongstad sludge and MudSplit1

Mongstad oil sludge was tested under various conditions. The analyzed upper phase of the samples in Table 12 showed a high volume percentage of oil. The upper phases consisted of ≥ 90 % oil, and most samples were free of water, indicating a high-quality oil. The volume percentage of solids was still too high to reach the standard of < 1 % solids and water. However, an unknown percentage of the volume percentage of solids might be salts, as the calculated volume percentage includes both suspended and dissolved solids. The analyzed upper phases in Table 12 all had a high oil content ranging from 90 – 96 %. There is no significant difference between the low or high dosage of MudSplit1 or N-Sep, which accounts for the differences in the volume percentage of oil.

The samples adjusted to pH 3.5 had a clear middle phase, where the expected water recovery was high. This is because NAs are not readily soluble in the aqueous phase at this pH. The samples in which the pH was not adjusted had a middle phase that visually seemed contaminated with hydrocarbons (Table 13). This assumption is also supported by the acid-base equilibrium reaction of NAs, as some NAs are quickly dissolved in the aqueous phase at pH 7.1 ($\text{pH} > \text{pK}_a$). This results in a high naphthenate and hydrocarbon content, as the naphthenates tend to carry hydrocarbons into the water. It should, however, be noted that the middle phase was not analyzed, and consequently, no OWR value was calculated.

The samples containing an upper phase with the highest percentage of oil were those heated to 60 °C and 90 °C. These samples include 1.1.1 to 1.3.1, 1.13.1, 1.15.1, and 1.16.1. There is no correlation between their chemical dosages. However, the observed decrease in oil percentage for those samples heated to 70 °C and 80 °C is difficult to explain and is probably due to sources of error. There is no logical explanation for the decrease between 70 and 80 °C and the increase at 90 °C.

Optimization of MudSplit1 dosage

As most samples in Table 12 resulted in successful separation with an upper phase of high-quality oil, lower dosages of MudSplit1 were tested. As presented in Table 14, samples with a MudSplit1 dosage of 0.05 % gave similar results as those samples with dosages ranging from 0.25 – to 1 %. This indicates that the chemicals have a minimal effect, or the effect is inhibited.

The samples where the pH was lowered to 3.5 showed a slightly more dependency on the chemical dosing. The upper phase consisted of a small amount of water until the dosage of MudSplit1 reached 0.2 %. The reason for this is unknown but might be an effect of the pH on the sludge system, resulting in poorer separation. It could also be that MudSplit1's function is affected by the increased proton concentration at this pH. Surfactants can behave differently to changes in pH based on the surfactant's ionic structure.

5.4.2 Mongstad sludge and MudSplit2

The effect of MudSplit2 on the demulsification of Mongstad sludge showed a similar effect as MudSplit1. Results in Table 17 show no presence of water in any of the samples and a slightly higher volume percentage of solids in some samples. The variation in the volume percentage of solids could be due to a positive chemical reaction or due to uncertainties related to the sampling or analysis.

5.4.3 Retort analysis of selected bottom phases

Selected bottom phases were analyzed by retort apparatus to determine the efficiency of the demulsification process. The bottom phases analyzed were from samples treated with MudSplit1 and MudSplit2 under the same conditions that made it possible to compare the effect of the chemicals. As presented in Table 16 and Table 19, the bottom phase consisted mainly of oil and water. The calculated OWR values for the samples range between 0.4 – 0.6, indicating

that the bottom phase consisted of a relatively low volume of oil, but higher than expected. This indicates that the demulsification process was not 100 % successful as some amount of oil remained in the bottom phase. The oil that remained in the bottom phase is believed to be due to heavy fractions (higher densities) of the oil, like asphaltene and resins, which tend to form solid particles and separate from the crude oil. The volume of solids in the bottom phase was also lower than anticipated. The samples treated with MudSplit1 and MudSplit2 gave no significant difference in the analyzed bottom phases and indicated no difference in the destabilization efficiency of the chemicals.

5.4.4 Effect of thermal and mechanical treatment

The effect of thermal and mechanical treatment without the use of chemicals was tested. The result in Table 20 shows an increased destabilization effect of the sludge going from 20 °C to 40 °C. Heating the samples decrease the sludge's viscosity and promote demulsification. After reaching approximately 40 °C, heavier paraffins like wax melts. Increasing the temperature further to 60 °C, showed no increased separation efficiency. The volume percentage of oil in the upper phase was 88 % at 20 °C, indicating that the sludge could be separated by only mechanical treatment at 2500 RCF. Applying heat and increasing the temperature of the samples to 40 °C and 60 °C, same results for the upper phases were obtained as those samples treated with chemicals in Tables 12, 14, and 17.

5.4.5 Summary of the effect of MudSplit chemicals on Mongstad sludge

The results of the demulsification efficiency of Mongstad sludge had varying visual separation degrees. The analyzed upper phases consists, in most cases, of the same amount of oil, where most range from 90 – to 96 %. Without using chemicals, the same results were obtained by only thermal and mechanical treatment. The separation effect observed in most samples is probably due to the viscosity reduction by thermal heating of the sludge samples, which is supported by mechanical treatment. It is believed that the effect of the added chemicals failed to be observed because of the “salting effect”. The ion composition of the water included in the sludge is not known but can have a dramatic negative effect on the efficiency of the surfactants. The content of salt ions, especially divalent ions, could affect the efficiency of the MudSplit chemicals. The salinity could be a reason why the effect of the chemicals is not observed by causing an inappropriate interaction between the chemicals and the sludge system. The inappropriate interaction between the chemicals and the sludge system could be further supported by the

analyses of the bottom phases. The retort analysis of the bottom phases in which samples were treated with MudSplit1 and MudSplit2 (Tables 16 and 19) were close to equal. This indicates that, either the chemicals have the same effect on the sludge, or that the chemicals have not fully interacted with the sludge.

Another hypothesis is that the MudSplit chemicals don't work or don't have a significant effect on the complicated sludge system. However, this needs further testing before it can be concluded. The viscosity drop by the addition of MudSplit is present, so it is clear that a form of reaction occurs.

5.5 Main experiment Brenda sludge

5.5.1 Brenda sludge and MudSplit1

Treatment of the samples presented in Table 22 gave visually great separation efficacy, and all the samples were graded 3 according to Table 8. The upper phase consisted of two parts, one less dense phase and one denser phase. The less dense phase was analyzed by the retort apparatus. This phase was of low volume (<50 mL) and was therefore presented as a mass percentage in the results. The analyzed upper phases showed the same results and did not distinguish significantly from samples 1.0.1 and 1.0.2, which were treated by only thermal and mechanical treatment (no addition of MudSplit). This indicates that the effect of MudSplit1 is low or negligible. The denser phase was an emulsified fluid of high viscosity, consisting of oil and a significant amount of water and solids. This phase was not analyzed by retort analysis but by a flame test. During the flame test, a small amount of the fluid was burned. The fluid did not ignite, indicating that it contained an undesirable amount of water. It was also possible to visually see that the fluid contained a considerable amount of particles. The reason for these two-phased upper phases is probably due to ineffective destabilization of the sludge by the MudSplit1 chemical. Insufficient destabilization could also be supported by the fact that untreated Brenda sludge contained 40 % oil (Table 11) which does not correspond with the volume of the upper phase after treatment.

The modification of pH did not give a better separation efficiency. At pH 3.5 (samples 1.6.1 and 1.6.2), the visual separation efficiency was equal to those at neutral pH. The upper phase was tested with a flame test and contained a considerable amount of water. At pH 10 (samples 1.7.1 and 1.7.2), the upper phase was of visually larger volume, and the bottom phase's volume

was smaller and more compact. The upper phase was tested with a flame test and contained a significant amount of water. In addition, the upper phase consisted of many particles, which could be seen visually. The sludge did not show better separation efficiency by either high or low pH. Compared to Mongstad sludge, Brenda sludge required double the amount of HCl and NaOH to reach the desired pH. This indicates a stronger buffer capacity of Brenda sludge and that the sludges' properties differ significantly.

The middle phase in all samples was expected to give high water recovery. It was contaminated by flocks, but the phase was relatively transparent in comparison to Mongstad sludge which needed the pH to be lowered to get a transparent middle phase. An explanation for this could be the sludge's content of higher molecular weight NAs, which are less soluble in the aqueous phase. At elevated pH of 10, the middle phase was still transparent, indicating that the NAs in this sludge do not readily partition between the oil and water phase.

5.5.2 Brenda sludge and MudSplit6

The visual separation efficiency of the sludge treated with MudSplit6 gave similar results as those treated with MudSplit1. The upper phase of the sample consisted of two phases, one less dense and one denser. The less dense phase was analyzed by retort analysis, and the results for all the treated samples were similar. The increase in dosage had no significant effect. However, a slight increase in the mass percentage of oil and a slight decrease in the mass percentage of water and solids were observed. The increased mass percentage of oil by increased dosage is so small that it is difficult to determine if it is an observed effect of the chemical or a random error.

5.5.3 Summary of the effect of MudSplit chemicals on Brenda sludge

The demulsification efficiency of Brenda sludge was limited. An apparent effect of the tested MudSplit chemicals was not observed based on the retort analysis of the separated upper phases. The sample that was only thermal and mechanical treated gave the same results as those that were treated with chemicals in combination with thermal and mechanical treatment. The reason why the effect of the chemicals failed to be observed could be due to the presence of salt ions, which could dramatically decrease the effect of the MudSplit chemicals. Another factor could be the age of the sludge. The sludge has been stored untreated for about six years. The properties of the emulsion may have changed, which negatively affects the demulsification efficiency.

Such a long storage time could have led to a smaller droplet size distribution and stronger interfacial films surrounding the droplets, making the emulsion more stable and difficult to treat.

5.6 Summary of the destabilization efficiency of crude oil sludges

The destabilization and demulsification process of crude oil sludges are challenging, and it is evident that several factors affect this process. Through the analysis of the results obtained during the experiment, some interesting facts connected with the chemical, thermal and mechanical processes were recorded. The results for Mongstad sludge showed that it was mainly the temperature combined with mechanical centrifugation that promoted the destabilization of this sludge. Gravitational separation by centrifuge is an essential factor in the separation process, enhancing the settling velocity. In addition, the effect of heat energy promotes the separation efficiency according to Stokes law. This can be explained by the fact that heat energy reduces the system's viscosity, increasing droplet collision rate and easing droplet coalesce. Also, by easing droplet coalesce, droplet size increases, making the density differences between oil and water larger. According to Stokes law, this enhances the separation. The effect of pH enhanced the separation efficiency, making the middle phase less contaminated, with possible high water recovery.

The effect of the chemicals was not clearly observed by the chosen methodology. This could be due to the complex internal structure of this waste. The sludge probably contains a significant concentration of salts, which could inhibit the effect of the chemicals. The sludge also contains some percentage of functional molecules like wax, asphaltenes and resins, which have been shown to make strong interfacial films and hinder droplet coalesce. They are also shown to promote steric stabilization of the emulsion. The combination of salt ions and functional molecules both facilitates the diminished or inhibited effect of the chemicals. Another reason could be due to insufficient dosing or mixing. Crude oil naturally contains compounds with surfactant properties (NAs, asphaltene, and resins) in varying concentrations. The concentration of these compounds correlates with the chemical dosage required for the demulsifier to neutralize the stabilization effect of these compounds. Therefore, the dosing performed during this experiment might be insufficient if the sludge contains heavy concentrations of natural surfactants. Insufficient mixing could also be one reason why the effect of the chemicals is not observed. The chemicals need sufficient mixing time to react with the sludge system, and the

time needed for this reaction to occur is unknown. The sludge's complex composition might account for the longer mixing time required.

Brenda sludge showed to be even more challenging to destabilize. The reason for this could be the presence of salt ions and functional molecules. Another reason, or an additional reason, could be the age of the emulsion. Achieving a successful demulsification has been reported as challenging when treating aged emulsions. This is because the emulsion properties tend to change after being untreated for an extended period.

Comparing Mongstad and Brenda sludge is challenging due to the significant differences in the sludge systems. Both sludges have a complex internal structure with different properties, which could be illustrated by how they were affected differently by the addition of HCl and NaOH. This supports the statement that there is no universal treatment option for this waste, and each kind of sludge needs one specific treatment design.

The effect of increased gravitational force was not investigated. The centrifugal operation parameters were fixed at 2500 RCF with a centrifugal retention time of 4 minutes. It should be noted that higher RCF should, according to Stokes law, increase the separation efficiency. To decrease the energy consumption of the treatment process, efficient separation while including low RCF in combination with low retention time is favorable.

6. Conclusions

The destabilization of crude oil sludges was investigated. The objective of the thesis was to investigate conditions for obtaining a three-phase separation, including an upper phase, a middle phase, and a bottom phase. The objective of obtaining an upper phase with a high-quality oil was successfully achieved. However, the refinery standard of achieving oil with less than 1 % water and solids has not yet been achieved within this research. Based on the analysis of the results of this research, the following conclusions can be drawn:

- The pre-screening method with small sample volume proved to be insufficient for evaluating the destabilization efficiency. This is because the method does not give an insight into the quality of the separated phases. In addition, the destabilization efficiency may seem worse than it was, giving a misleading result.
- Three-phase separation was obtained by both types of sludge (Mongstad and Brenda sludge). The destabilization of Mongstad sludge was considered more successful because most samples included an upper phase with a large volume percentage of oil. The bottom phase contained a noticeable volume of oil, which indicate that the demulsification was not fully completed. Brenda sludge turned out to be more challenging to achieve an efficient demulsification. The retort analysis of the upper phases showed a high mass percentage of oil and a low percentage of water and solids, but the phase was of low volume. However, the upper phase in this sludge consisted of two phases. The second phase (which was tested by flame test) contained emulsified oil with significant amounts of water and solids. Therefore, the upper phase, which was of relatively high-quality oil, was of low volume, indicating that the demulsification was incomplete.
- Temperature showed to be the most crucial factor for the destabilization of the sludge. Heat energy reduces the viscosity of the sludge system and increases coalescence. The effect of heat energy was obtained for Mongstad sludge and also for Brenda sludge, but less efficiently. The results presented for Mongstad sludge indicate that the heat energy combined with mechanical centrifugation accounted for the overall separation efficiency.

- The effect of the MudSplit chemicals was not distinctly observed during the test conditions of the methodology. No comprehensive correlation between small or larger chemical dosages was found. In addition, the same results for the volume percentage of oil, water, and solids in the upper phases were achieved with and without using chemicals. The unobserved effects of the chemicals could be due to the salinity of the sludge, which inhibits the chemicals from efficiently reacting with the sludge system. Another reason could be insufficient chemical dosing or mixing, which leaves the emulsion not destabilized.
- The effect of pH was visibly obtained in Mongstad sludge and proved to be an enhancing factor. This is probably due to the middle phase being contaminated by NAs and hydrocarbons at neutral pH, and by lowering the pH to 3.5 ($\text{pH} < \text{pK}_a$), the NAs become less soluble in the aqueous phase. The effect of pH was not observed in Brenda sludge.
- No concluding remarks could be made certain of the effect of aging. By comparing Brenda sludge (aged) with Mongstad sludge (fresh), it appears that the aging effect makes the destabilization process for Brenda sludge more difficult. However, the characteristics of the sludges are different, which could explain the destabilization efficiency differences. A hypothesis in correlation with the literature is that the Brenda sludge was more challenging to treat due to its age.

7. Future research

Based on suggestions from the supplier and the low sampling volume available during the research, the experiment was performed quite broadly concerning the experimental conditions.

The following recommendations are suggested for further studies:

- A thorough analysis of the properties of sludges is recommended to be the first step in the treatment process of this waste. The analysis should include a quantification of the crude oil contained in the sludge to determine its fraction of saturates, aromatics, resins, and asphaltene. This could give a better understanding of the stability of the sludge.
- Rheological measurements of the sludge's rheological properties could help better understand its complex structure and improve the sludge handling performance.
- It is recommended to measure the salinity of the sludge before starting the treatment process with demulsifiers.
- Detailed pH testing should be performed to find an optimum pH range specified for the sludge's composition. The effect of pH on the MudSplit chemicals should also be considered.
- A thorough investigation of sufficient chemical dosing is recommended. In addition, an investigation of mixing time is suggested to allow the complex sludge system to react appropriately with the chemicals.
- Performing a thorough investigation of optimal centrifugal parameters is suggested, including optimization of RCF and retention time.

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Appendix 1 – Preparation of chemical solutions

Diluted MudSplit was prepared as described below:

Diluted MudSplit (1:10) was prepared by mixing 10 mL of concentrated MudSplit with 90 mL of tap water, resulting in a total of 100 mL diluted MudSplit. The sample was shaken to a homogenous solution.

N-Sep solution was prepared as described below:

0.5 g of N-Sep was dissolved in 200 mL lukewarm tap water. The mixture was shaken in several rounds for a total time of one hour.

Appendix 2 – Description of dosing

In sample, where:

volume of every sample in the main experiment equals to 200 mL

0.05 % dosing is equivalent to 1 mL of diluted MudSplit

0.1 % dosing is equivalent to 2 mL of diluted MudSplit

0.15 % dosing is equivalent to 3 mL of diluted MudSplit

0.2 % dosing is equivalent to 4 mL of diluted MudSplit

0.25 % dosing is equivalent to 5 mL of diluted MudSplit

0.5 % dosing is equivalent to 10 mL of diluted MudSplit

0.75 % dosing is equivalent to 15 mL of diluted MudSplit

1 % dosing is equivalent to 20 mL of diluted MudSplit

Appendix 3 – Equations for mass percentage

Mass percentage of oil, water, and solids was calculated by the following equations:


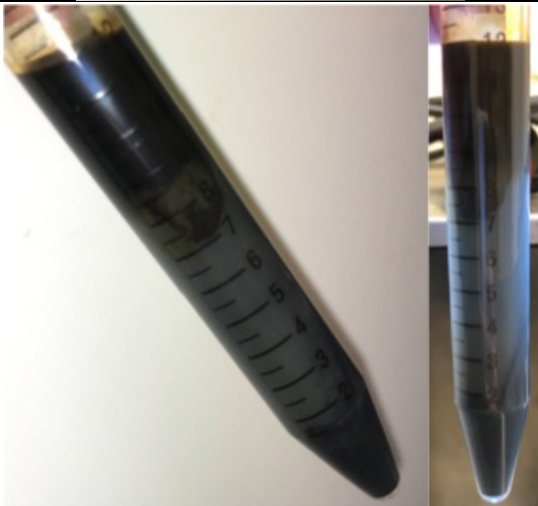

$$\text{Mass \% oil} = \frac{\text{Mass of oil collected (g)}}{\text{Mass of total sample (g)}} * 100 \quad \text{Equation 15}$$

$$\text{Mass \% water} = \frac{\text{Mass of water collected (g)}}{\text{Mass of total sample (g)}} * 100 \quad \text{Equation 16}$$

$$\text{Mass \% solids} = \frac{\text{Mass of solids collected (g)}}{\text{Mass of total sample (g)}} * 100 \quad \text{Equation 17}$$

Appendix 4 – Visual separation grade scale for pre-screening

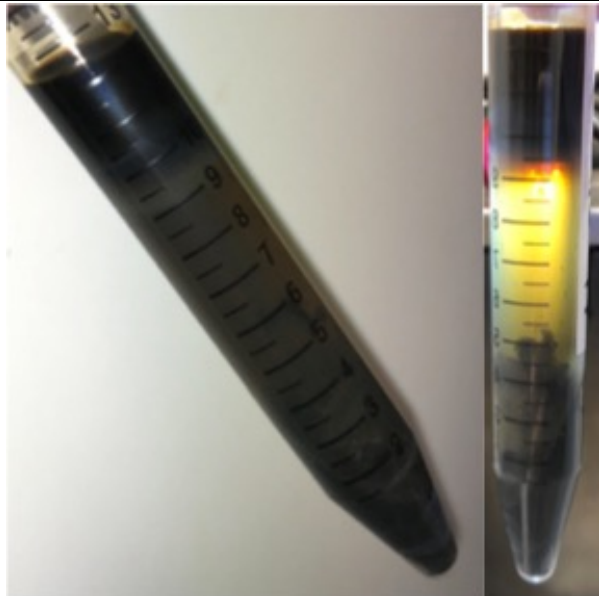
Table 26 Visual separation grade scale for pre-screening samples

Grade/description	Visual example
<p>1 No change and/or slightly visible changes</p>	
<p>2 Separation without clearly defined phases. Visible upper phase, but not clearly separated middle phase. Slightly visible bottom phase.</p>	
<p>3 Three-phase separation without clearly defined phases. Visible upper phase, visible middle phase which is turbid. Visible bottom phase.</p>	

4 Three-phase separation with defined phases. Defined upper phase. Middle phase is slightly turbid and is contaminated by small flocks. Defined bottom phase.








5 Perfect three phase separation with clearly defined phases. Middle phase is transparent and not contaminated by flocks. Defined bottom phase.



Appendix 5 – Pre-screening of Mongstad sludge

Pre-screening of Mongstad oil sludge by thermal heating, addition of MudSplit1 and centrifugation. Pictures of samples is presented in Table 27, the corresponding dosage is marked in the top left corner.

Table 27 Pre-screening: destabilization of Mongstad oil sludge by MudSplit1

 <p>0.05 %</p>	 <p>0.25 %</p>	 <p>0.5 %</p>
 <p>0.75 %</p>	 <p>1 %</p>	

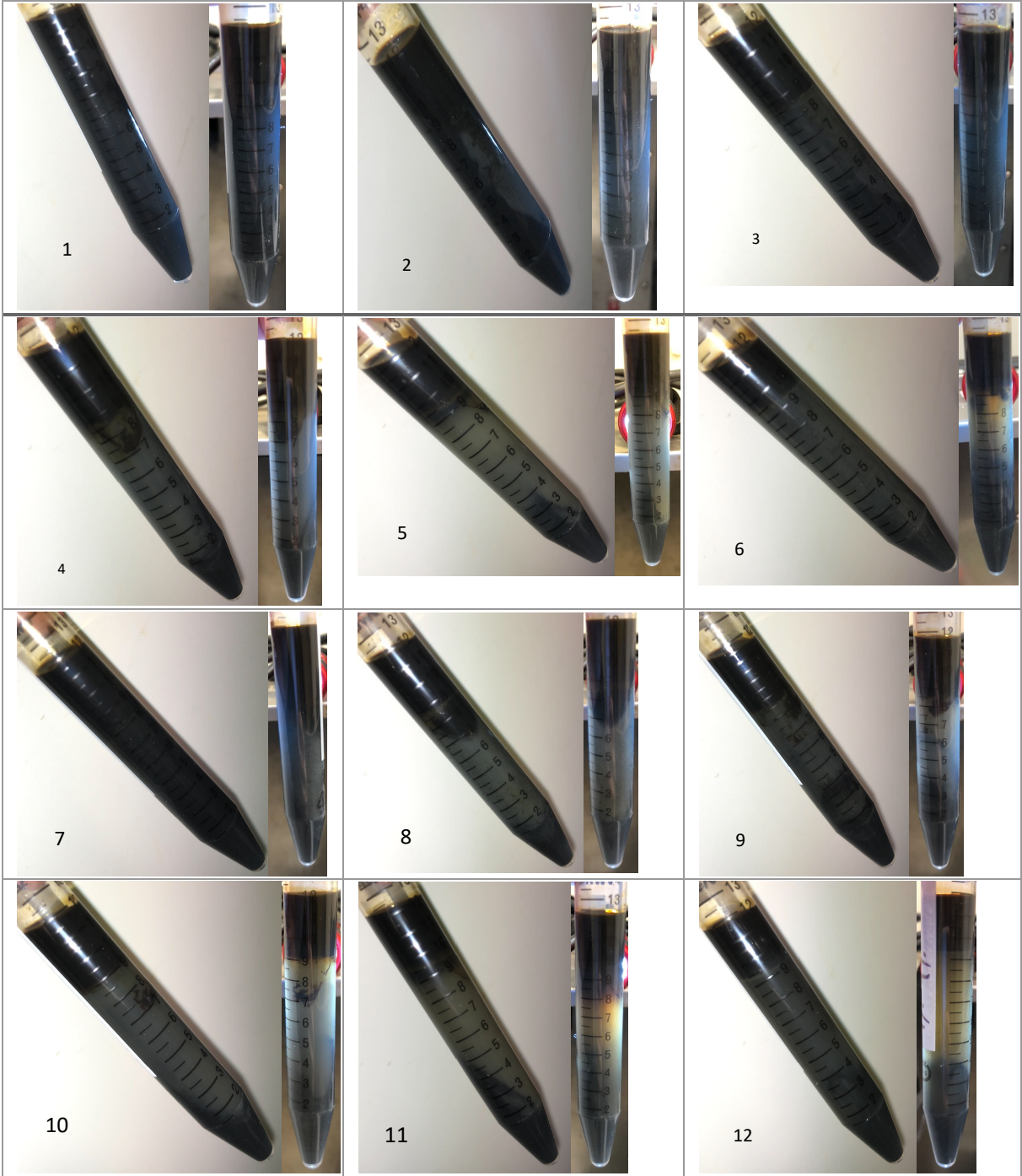
Pre-screening of Mongstad oil sludge by thermal heating, addition of MudSplit2 and centrifugation is presented in Table 28. The corresponding dosage is marked in bottom left corner.

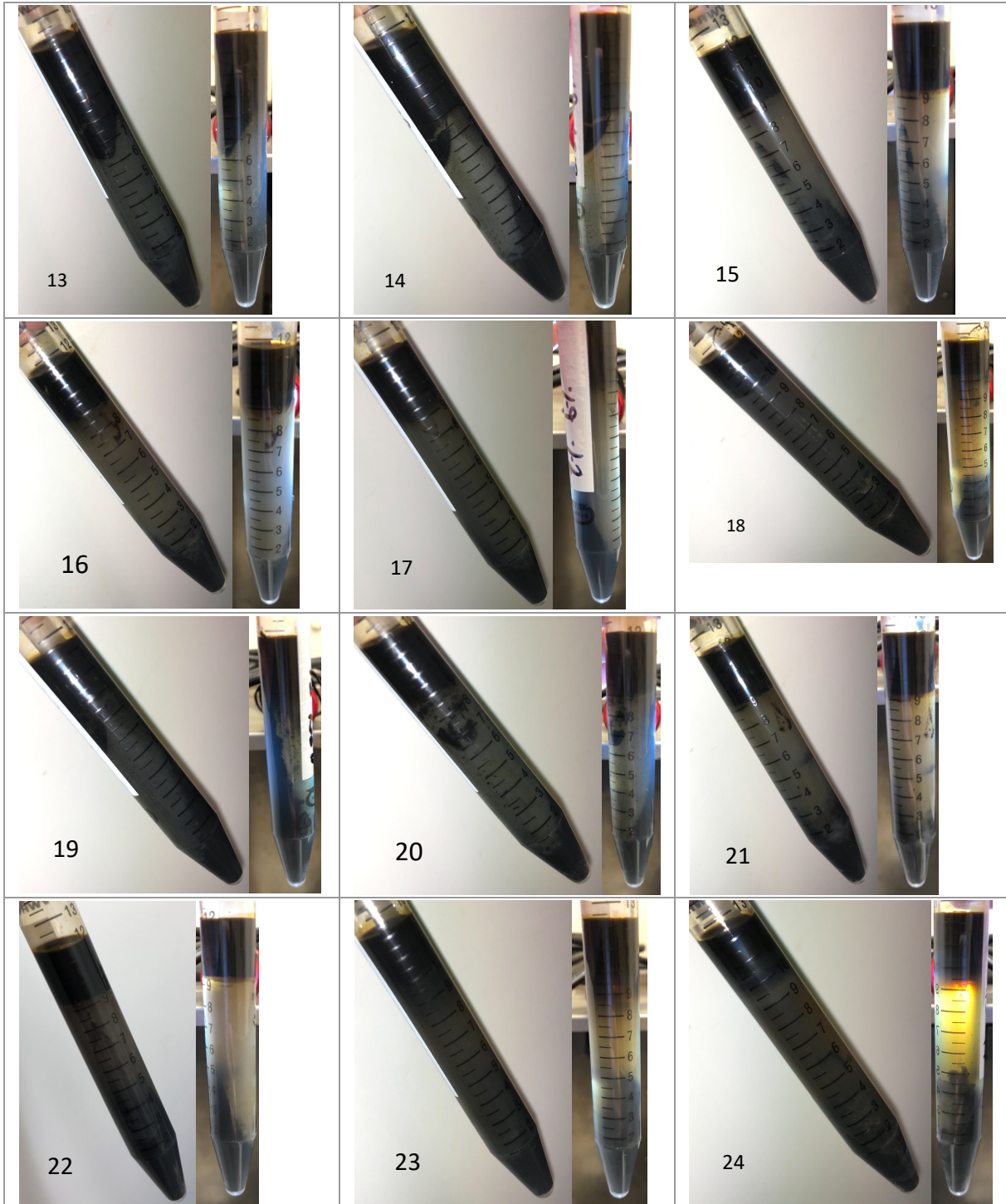
Table 28 Pre-screening: destabilization of Mongstad oil sludge by MudSplit2



Pre-screening of Mongstad sludge by MudSplit1 in combination with N-Sep at various concentrations is presented in Table 29. The samples are marked with sample number, which is placed in the bottom left corner of the picture.

Table 29 Destabilization of Mongstad oil sludge by MudSplit1 in combination with N-Sep at various concentrations

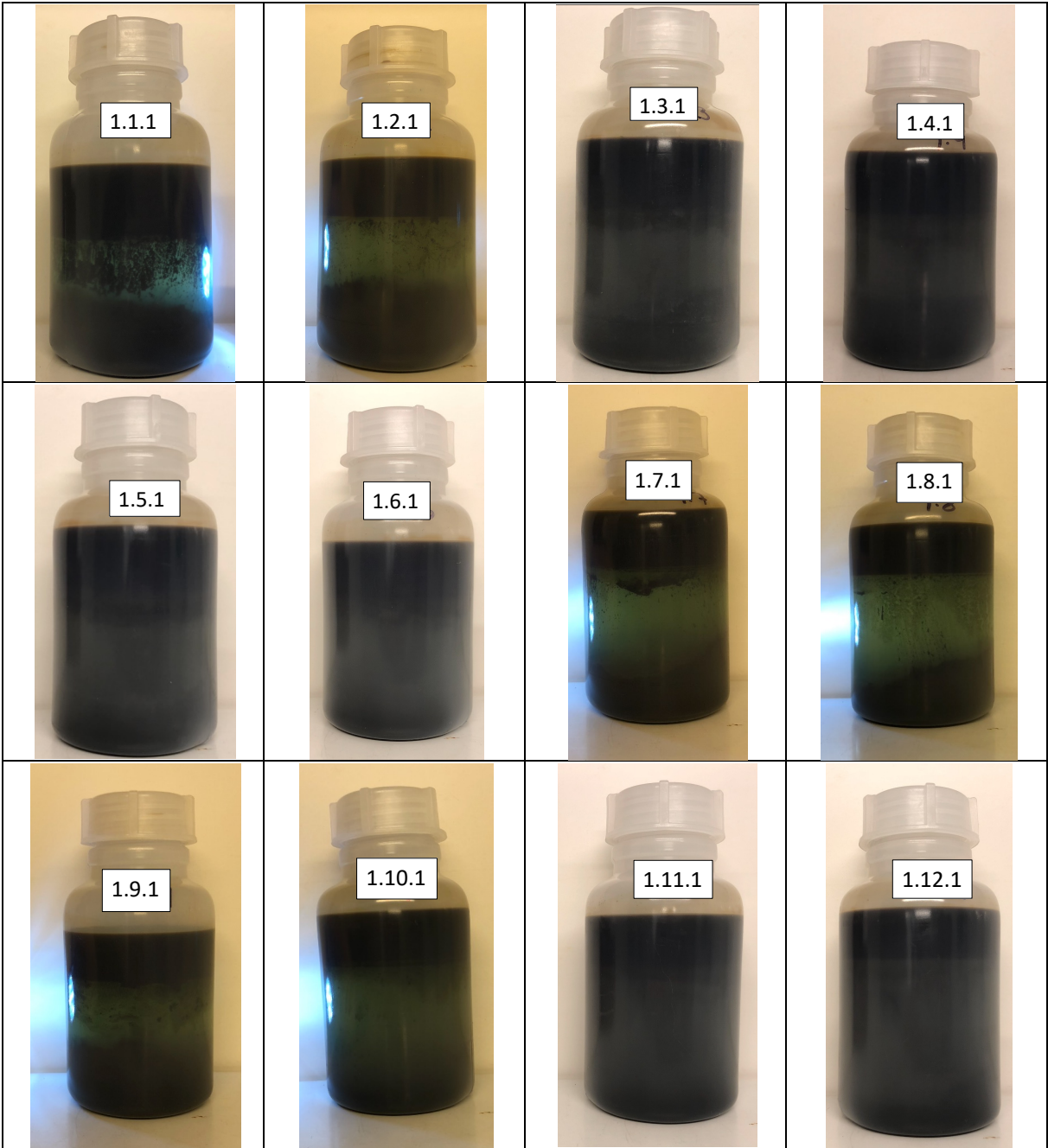




Appendix 6 – Destabilization of Mongstad sludge

Destabilization of Mongstad sludge by MudSplit1 in various conditions according to Table 2, is presented in Table 30 and Table 31.

Table 30 Destabilization of Mongstad sludge by MudSplit1 & N-Sep under various conditions, parallel 1



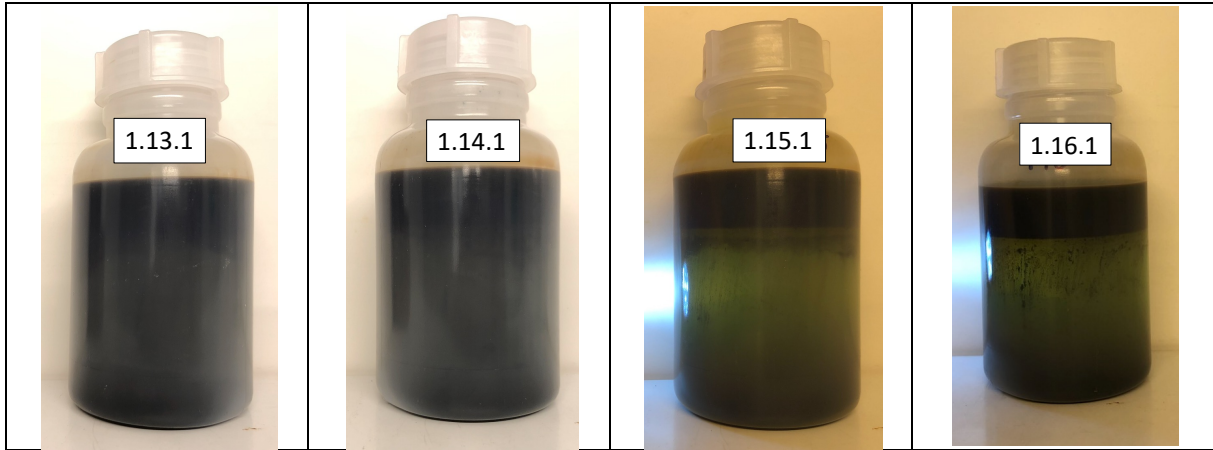
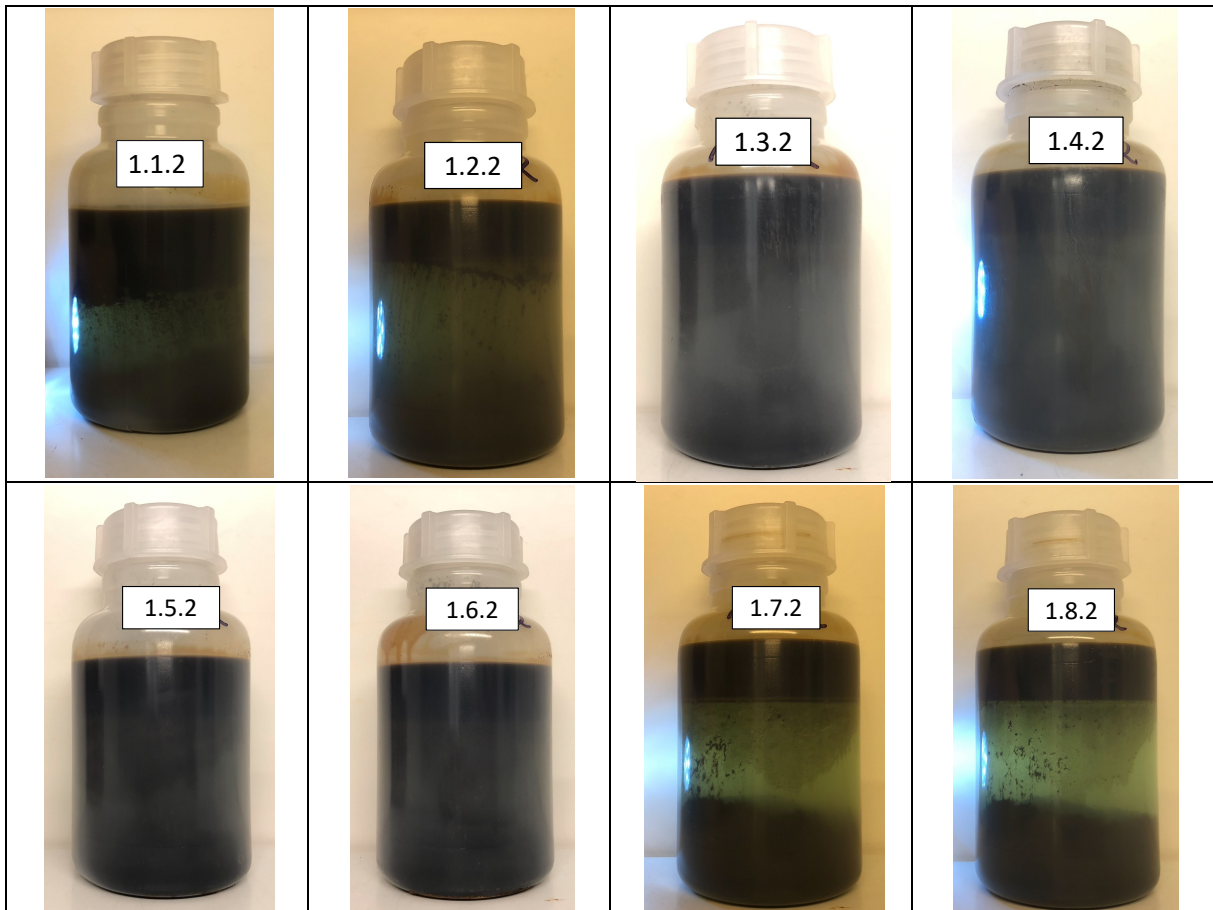
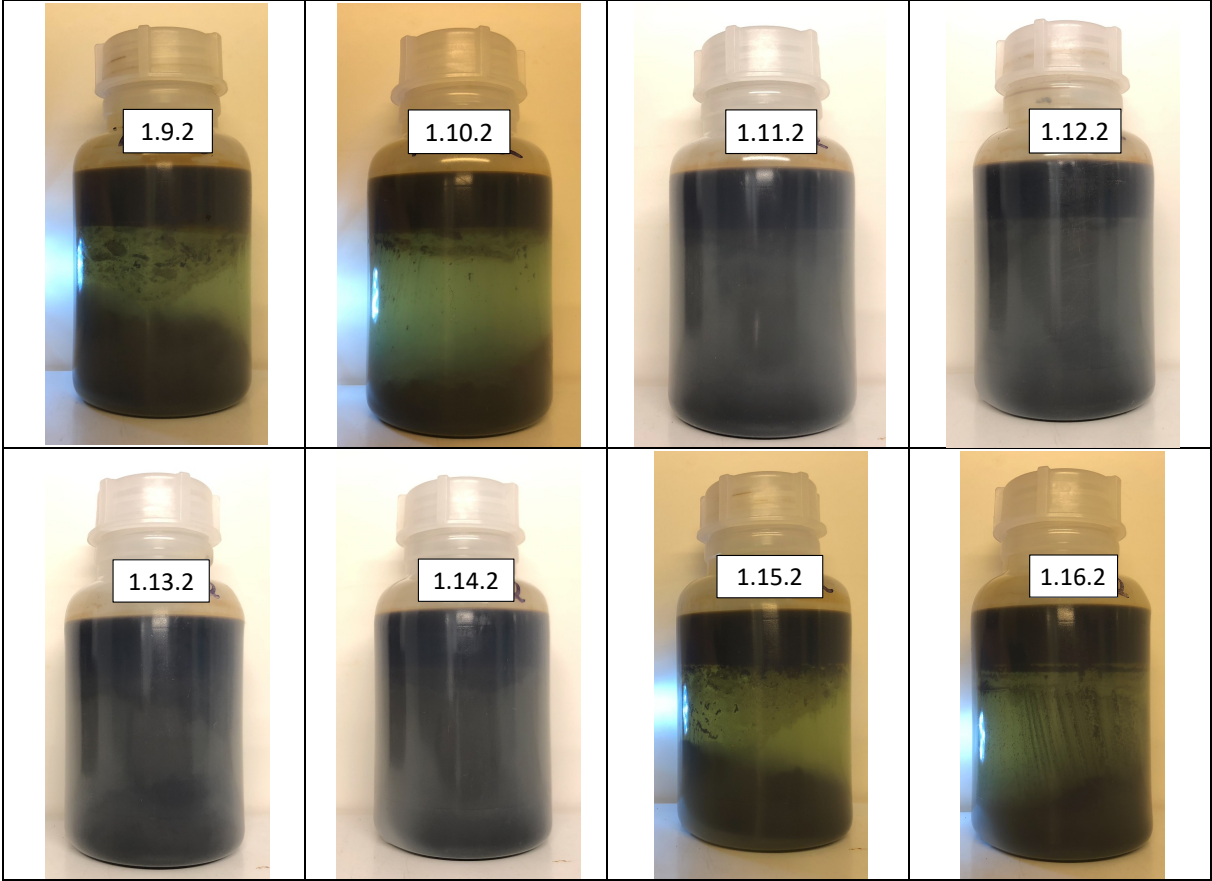


Table 31 Destabilization of Mongstad sludge by MudSplit1 & N-Sep under various conditions, parallel 2





Destabilization of Mongstad sludge according to conditions described in Table 3 is presented in Table 32 and Table 33.

Table 32 Destabilization of Mongstad sludge by optimized dosage MudSplit1 & N-Sep, parallel 1

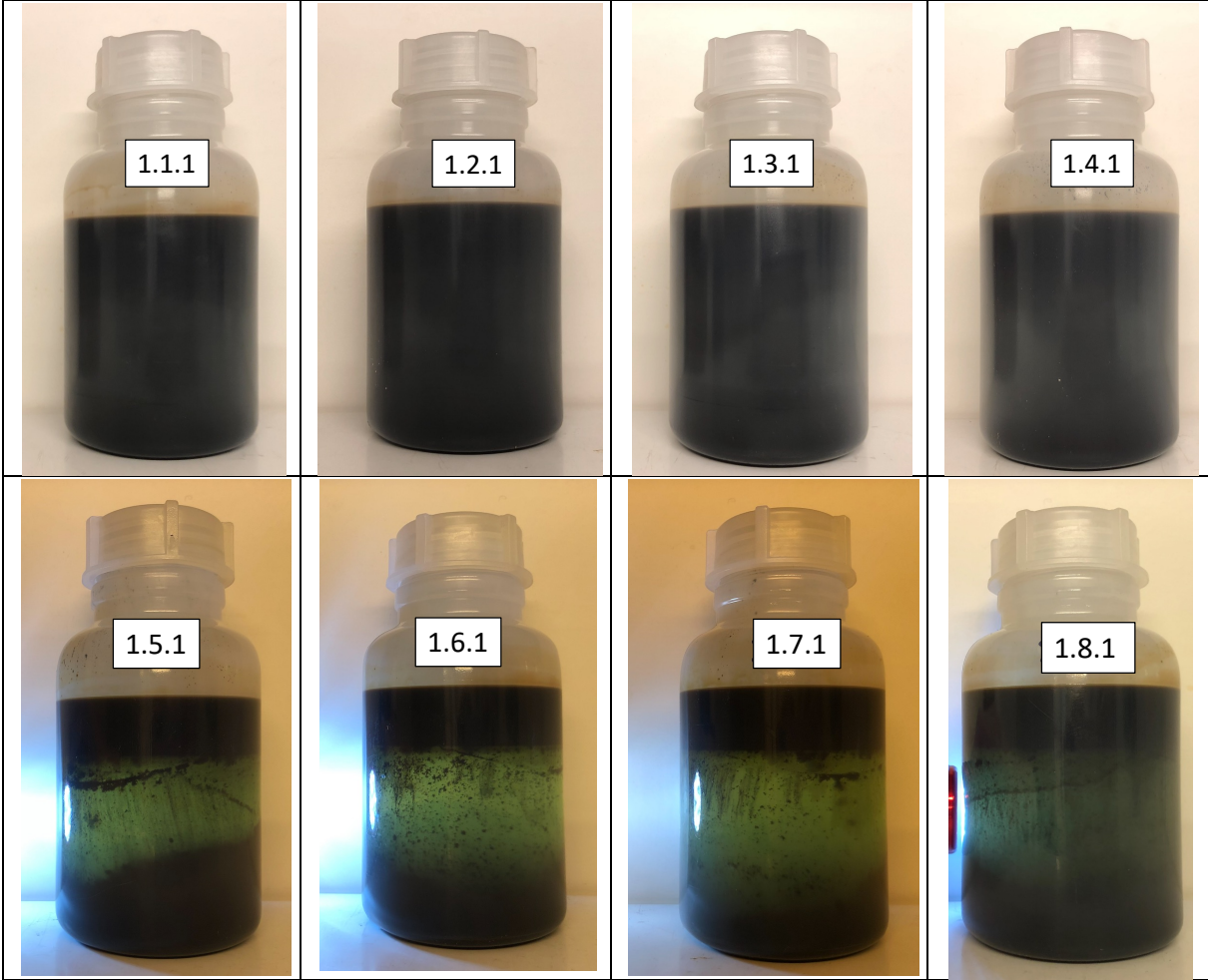
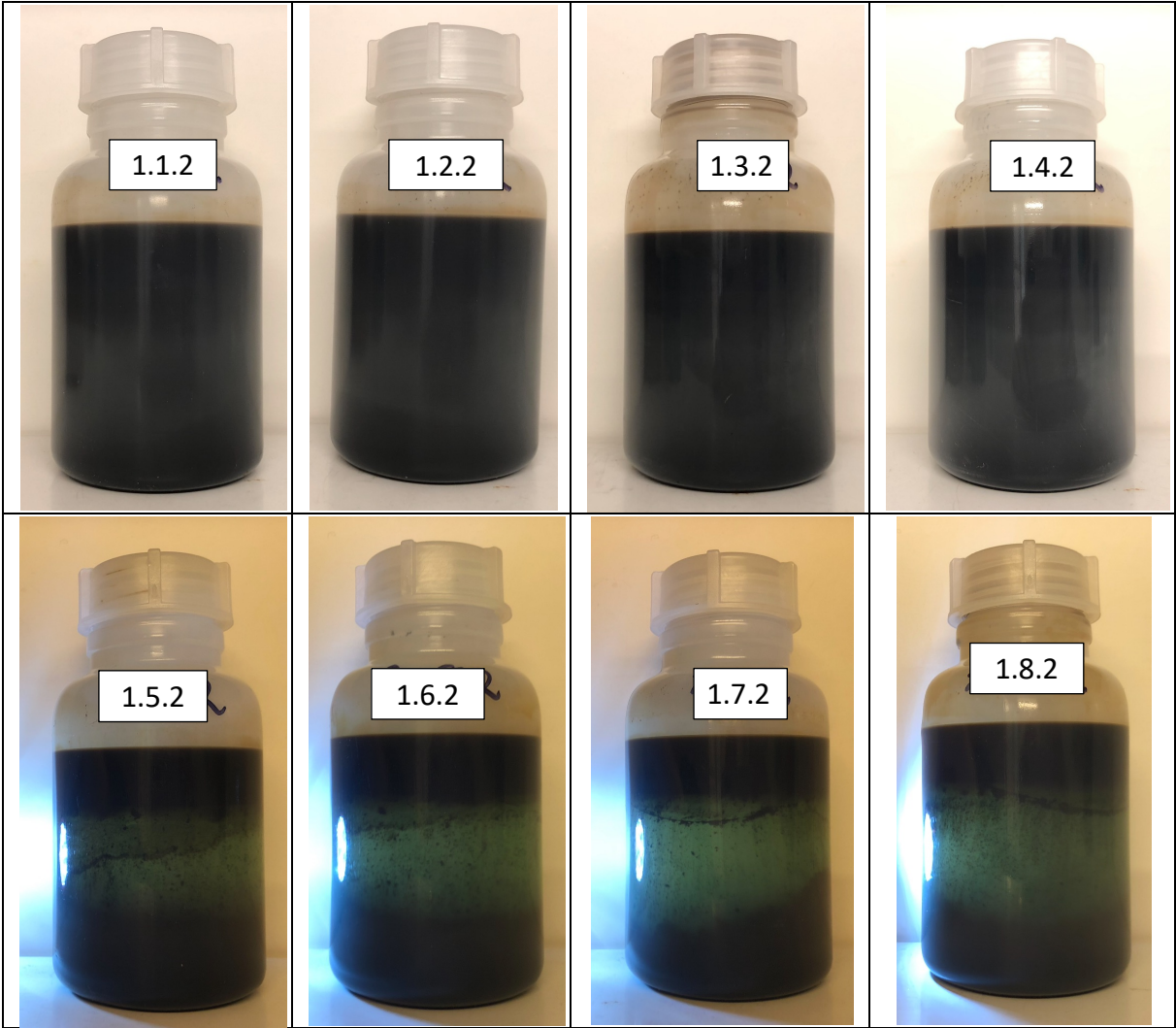


Table 33 Destabilization of Mongstad sludge by optimized dosage MudSplit1 & N-Sep, parallel 2



Destabilization of Mongstad sludge according to conditions described in Table 3 is presented in Table 34 and Table 35.

Table 34 Destabilization of Mongstad sludge by MudSplit2, parallel 1

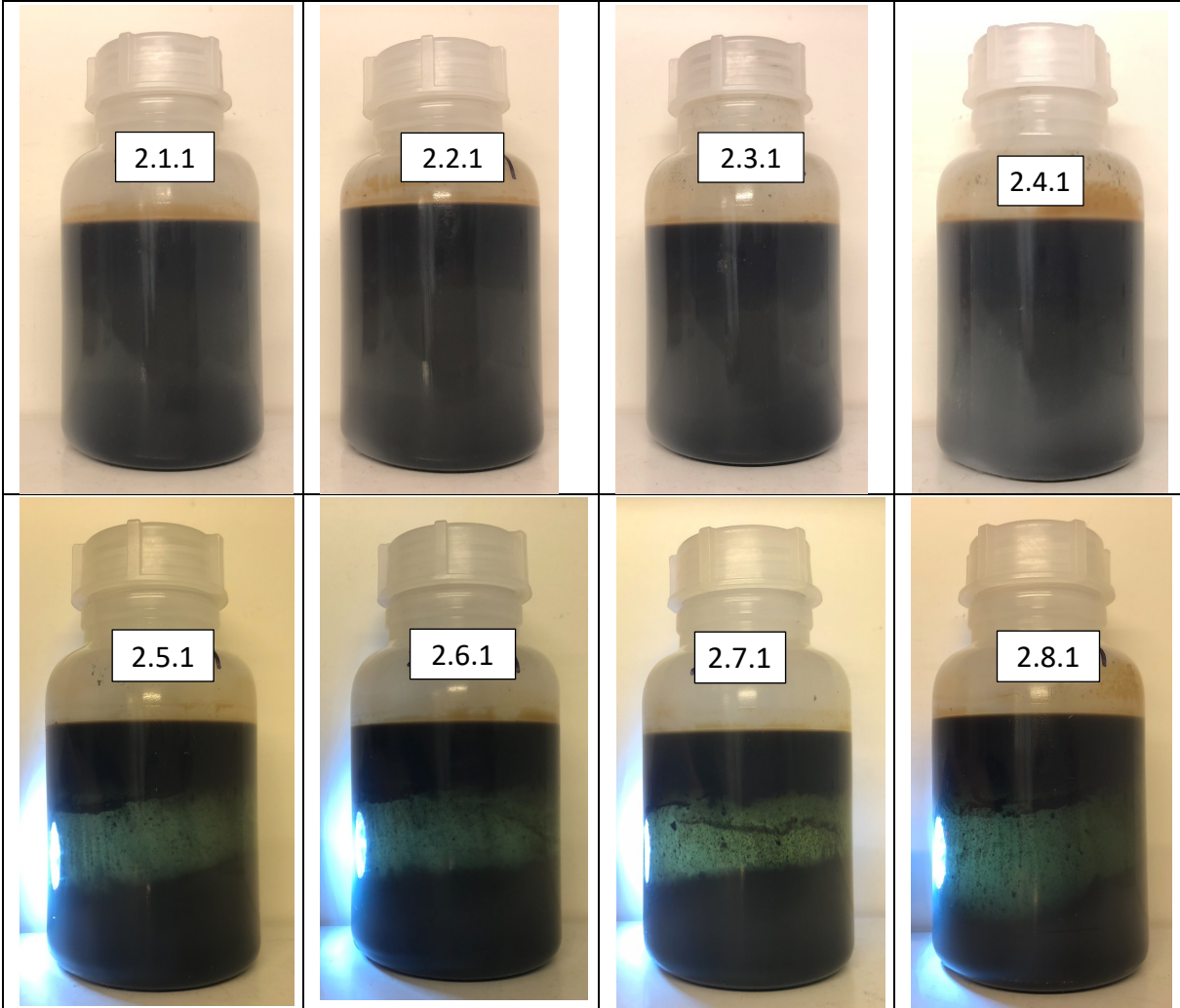
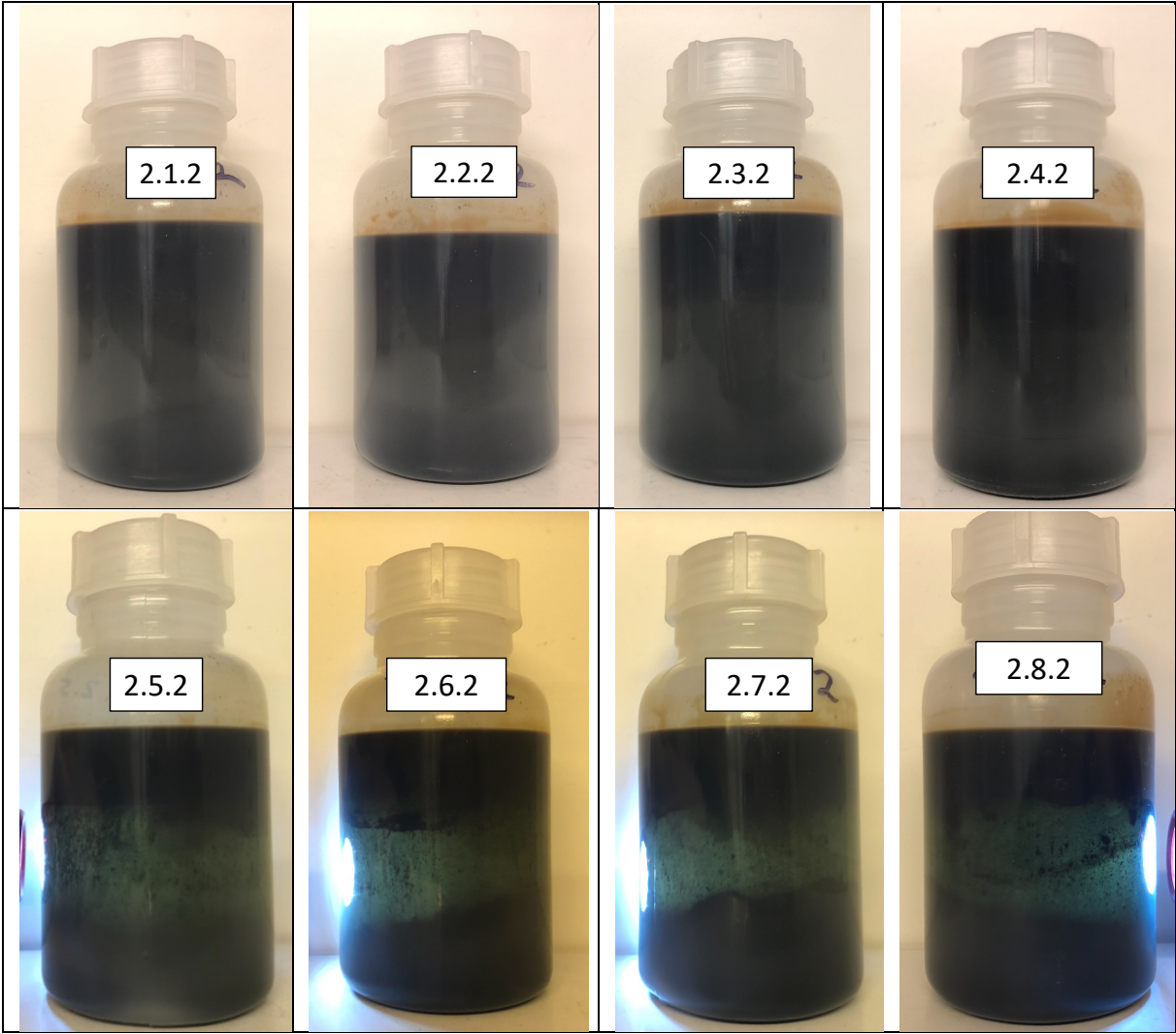


Table 35 Destabilization of Mongstad sludge by MudSplit2, parallel 2



Destabilization of Mongstad sludge without the use of chemicals is presented in Table 36 and Table 37.

Table 36 Effect of thermal and mechanical treatment, parallel 1

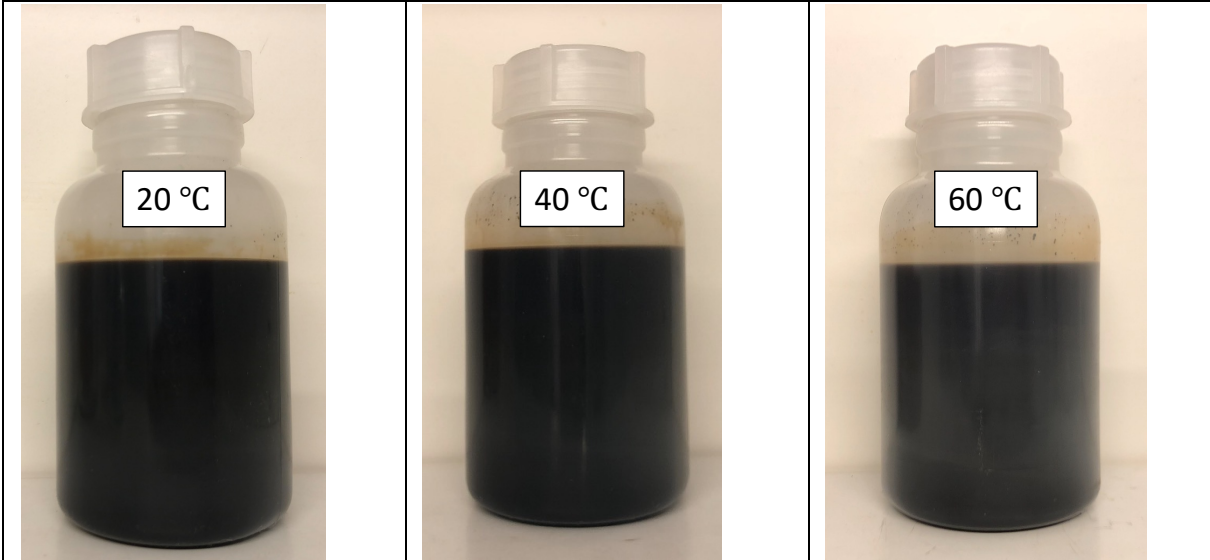
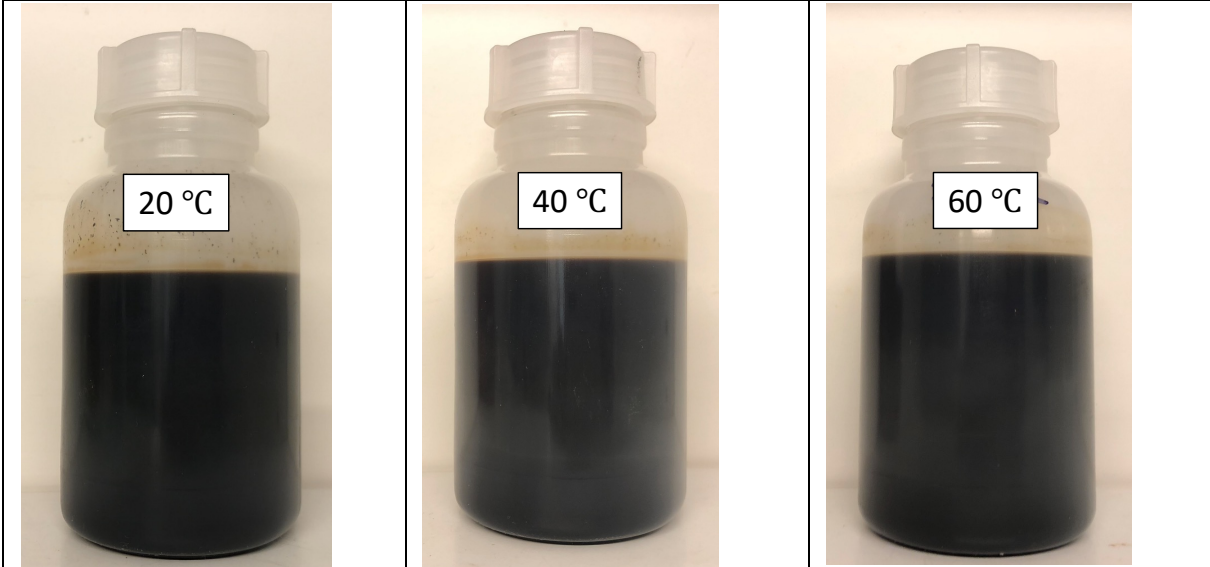


Table 37 Effect of thermal and mechanical treatment, parallel 2



Appendix 7 – Destabilization of Brenda sludge

Destabilization of Brenda sludge by MudSplit1 according to Table 4 is presented in Table 38 and Table 39. Destabilization by Mudsplit6 according to Table 5 is presented in Table 40 and Table 41.

Table 38 Destabilization of Brenda oil sludge by MudSplit1, parallel 1

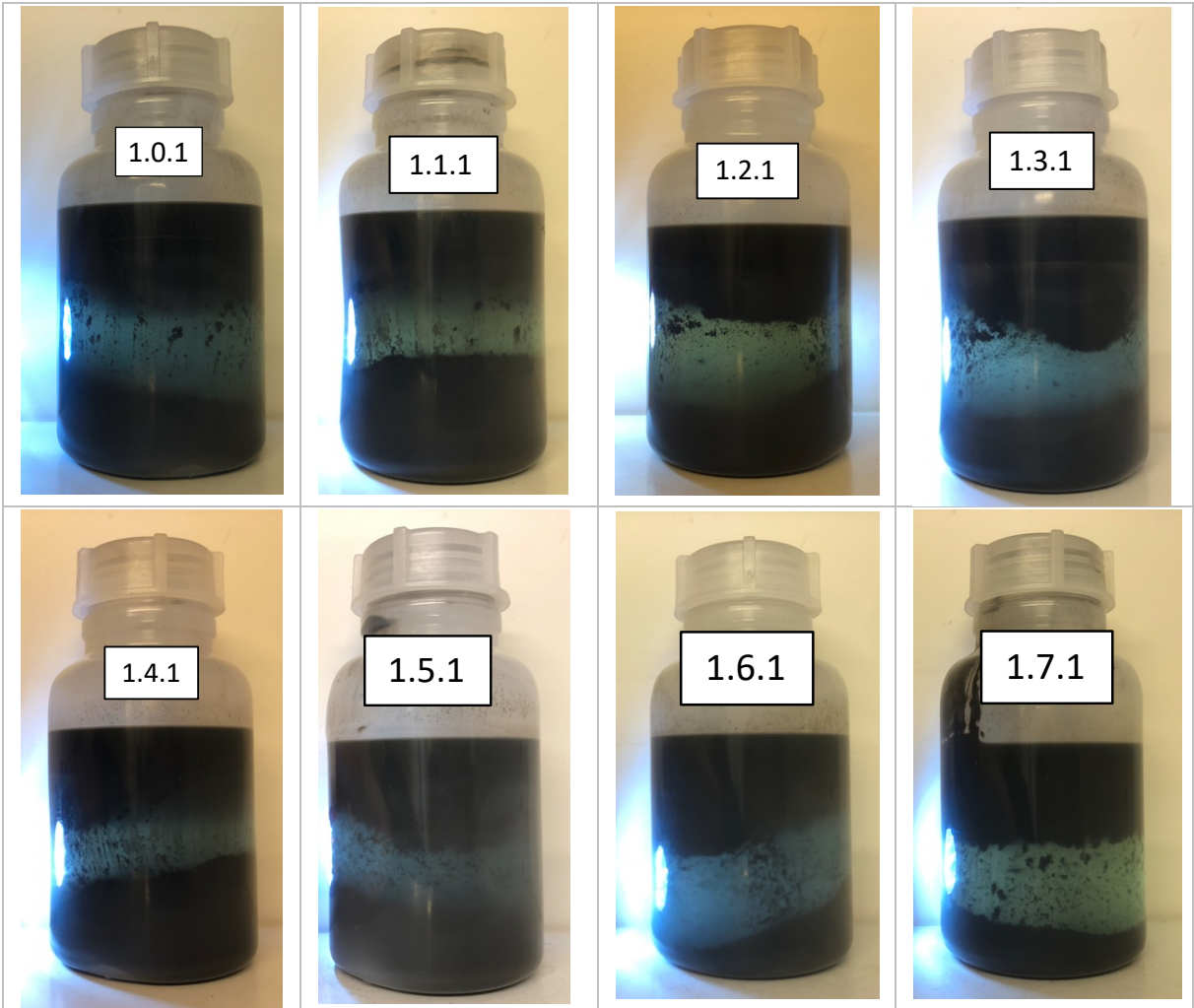


Table 39 Destabilization of Brenda oil sludge by MudSplit1, parallel 2

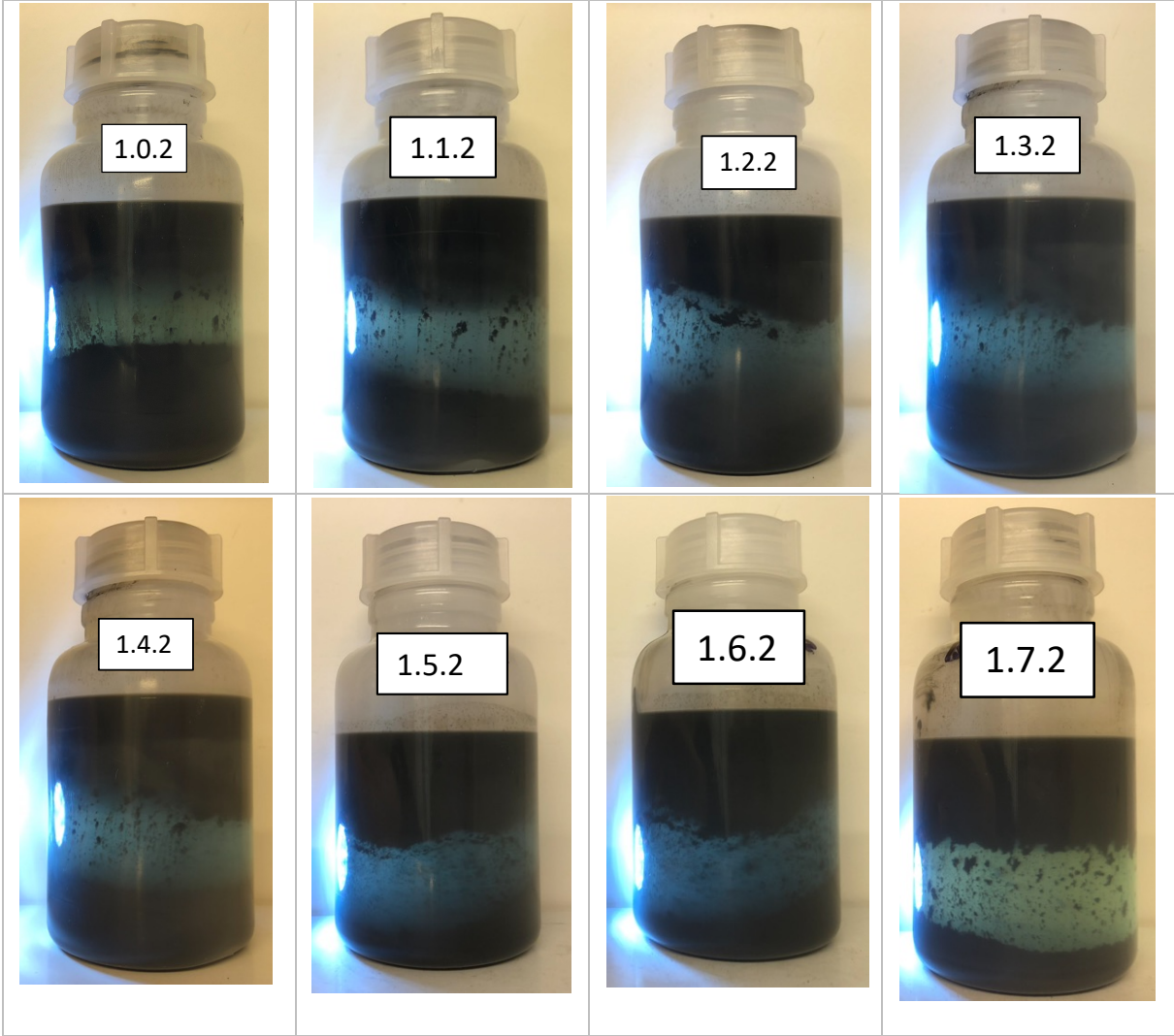


Table 40 Destabilization of Brenda oil sludge by MudSplit6, parallel 1

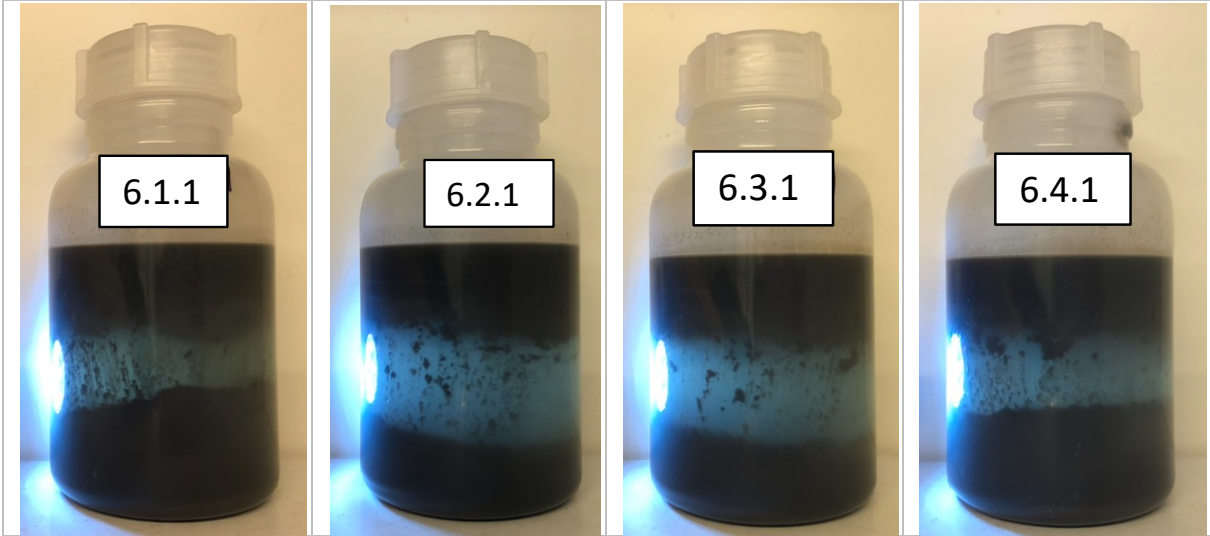
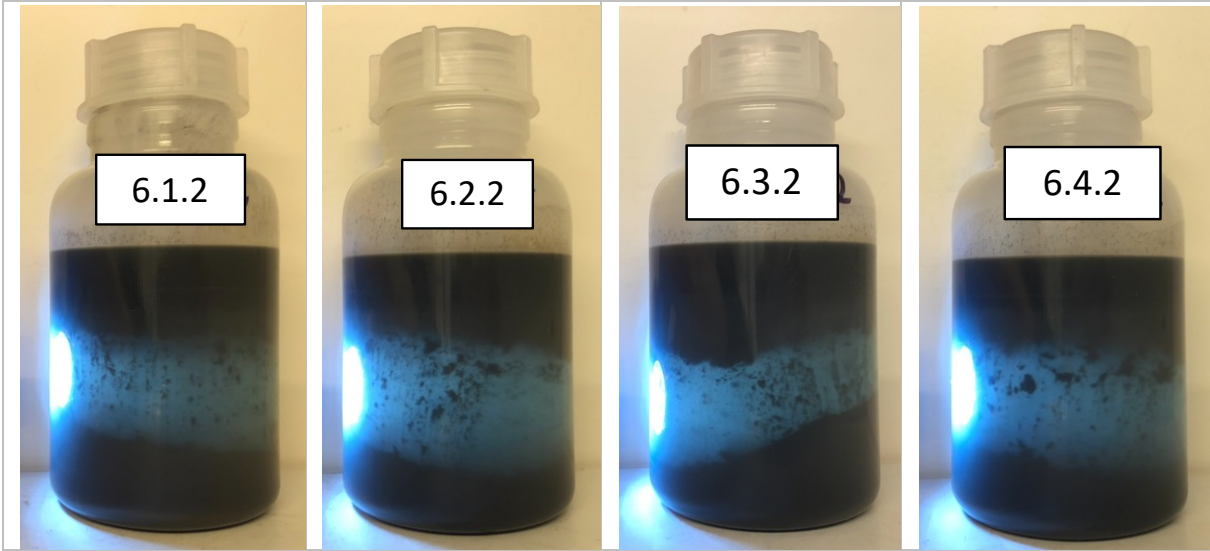


Table 41 Destabilization of Brenda oil sludge by MudSplit6, parallel 2



Appendix 8 – Data and calculations from retort analysis

Data and calculations from retort analysis of the upper phases for Mongstad sludge samples treated with MudSplit1 and MudSplit2:

Table 42 Calculation of volume percentage oil, water, and solids contained in the upper phase of Mongstad sludge treated with MudSplit1 in various conditions according to table 2.

Sample	Total liquid volume (mL)	Oil volume (mL)	Water volume (mL)	Volume % oil	Volume % water	Volume % solids	X	Y	OWR	Visual scale grade
1.1.1 and 1.1.2	47	47	0	94	0	6	100	0		3
1.2.1 and 1.2.2	47	47	0	94	0	6	100	0		3
1.3.1 and 1.3.2	47.5	47.5	0	95	0	5	100	0		2
1.4.1 and 1.4.2	46	46	0	92	0	8	100	0		2
1.5.1 and 1.5.2	46.5	46.5	0	93	0	7	100	0		2
1.6.1 and 1.6.2	46	46	0	92	0	8	100	0		2
1.7.1 and 1.7.2	46	45	1	90	2	8	97.8	2.2	45	4
1.8.1 and 1.8.2	46	46	0	92	0	8	100	0		4
1.9.1 and 1.9.2	45.5	45.5	0	91	0	9	100	0		4
1.10.1 and 1.10.2	45	45	0	90	0	10	100	0		4
1.11.1 and 1.11.2	46	46	0	92	0	8	100	0		2
1.12.1 and 1.12.2	45	45	0	90	0	10	100	0		2
1.13.1 and 1.13.2	47	47	0	94	0	6	100	0		2
1.14.1 and 1.14.2	47	45	2	90	4	6	95.7	4.3	22.5	2
1.15.1 and 1.15.2	47.5	47.5	0	95	0	5	100	0		4
1.16.1 and 1.16.2	48	48	0	96	0	4	100	0		4

Table 43 Calculation of volume percentage oil, water, and solids contained in the upper phase of Mongstad sludge treated with MidSplit1 according to table 3.

Sample	Total liquid volume (mL)	Oil volume (mL)	Water volume (mL)	Volume % oil	Volume % water	Volume % solids	X	Y	OWR	Visual scale grade
1.1.1 and 1.1.2	46	46	0	92	0	8	100	0	*	2
1.2.1 and 1.2.2	46	46	0	92	0	8	100	0	*	2
1.3.1 and 1.3.2	46	46	0	92	0	8	100	0	*	2
1.4.1 and 1.4.2	45	45	0	90	0	10	100	0	*	2
1.5.1 and 1.5.2	45.5	43	2.5	86	5	9	95	5	17.2	3
1.6.1 and 1.6.2	46	45	1	90	2	8	98	2	45	3
1.7.1 and 1.7.2	45.5	45	0.5	90	1	9	99	1	90	3
1.8.1 and 1.8.2	45.5	45.5	0	91	0	9	100	0	*	3

Table 44 Calculation of volume percentage oil, water, and solids contained in the upper phase of Mongstad sludge treated with MidSplit2 according to table 3

Sample	Total liquid volume (mL)	Oil volume (mL)	Water volume (mL)	Volume % oil	Volume % water	Volume % solids	X	Y	OWR	Visual scale grade
2.1.1 and 2.1.2	44	44	0	88	0	12	100	0		2
2.2.1 and 2.2.2	45	45	0	90	0	10	100	0		2
2.3.1 and 2.3.2	46	46	0	92	0	8	100	0		2
2.4.1 and 2.4.2	46	46	0	92	0	8	100	0		2
2.5.1 and 2.5.2	45	45	0	90	0	10	100	0		3
2.6.1 and 2.6.2	45	45	0	90	0	10	100	0		3
2.7.1 and 2.7.2	45	45	0	90	0	10	100	0		3
2.8.1 and 2.8.2	46	46	0	92	0	8	100	0		3

Data and calculations from retort analysis of the upper phases for Mongstad sludge samples treated with thermal heating and centrifugation:

Table 45 Calculation of volume percentage oil, water, and solids contained in the upper phase of Mongstad using thermal and mechanical treatment

Sample	Total liquid volume (mL)	Oil volume (mL)	Water volume (mL)	Volume % oil	Volume % water	Volume % solids	X	Y	OWR	Visual scale grade
20 °C	45	44	1	88	2	10	98	2	44	1
40 °C	46	46	0	92	0	8	100	0		1
60 °C	46	46	0	92	0	8	100	0		2

Data and calculations from retort analysis of the upper phases for Brenda sludge treated with MudSplit1 and MudSplit6:

Table 46 Calculation of volume percentage oil, water, and solids contained in the upper phase of Brenda sludge treated with MudSplit1 according to table 4

Sample	Total sample (g)	Oil (g)	Water (g)	Solids (g)	Mass % oil	Mass % water	Mass % solids	Visual scale grade
1.0.1 and 1.0.2	30.81	29.82	0.50	0.49	96.79	1.62	1.59	3
1.1.1 and 1.1.2	31.40	30.35	0.50	0.55	96.66	1.59	1.75	3
1.2.1 and 1.2.2	30.90	29.75	0.50	0.65	96.28	1.62	2.10	3
1.3.1 and 1.3.2	31.53	30.50	0.50	0.53	96.74	1.58	1.68	3
1.4.1 and 1.4.2	29.35	28.25	0.50	0.60	96.25	1.70	2.04	3
1.5.1 and 1.5.2	29.62	28.38	0.50	0.74	95.82	1.69	2.50	3

Table 47 Calculation of volume percentage oil, water, and solids contained in the upper phase of Brenda sludge treated with MudSplit6 according to table 5

Sample	Total sample (g)	Oil (g)	Water (g)	Solids (g)	Mass % oil	Mass % water	Mass % solids	Visual scale grade
6.1.1 and 6.1.2	27.62	26.35	0.50	0.77	95.40	1.81	2.79	3
6.2.1 and 6.2.2	26.03	25.00	0.50	0.53	96.05	1.92	2.04	3
6.3.1 and 6.3.2	31.71	30.93	0.20	0.58	97.54	0.63	1.83	3
6.4.1 and 6.4.2	30.04	29.32	0.20	0.52	97.60	0.66	1.73	3

Data and calculations from retort analysis of the bottom phases for Mongstad sludge samples treated with MudSplit1 and MudSplit2 according to Table 3:

Table 48 Calculation of volume percentage oil, water, and solids contained in the bottom phase of Mongstad sludge treated with MudSplit1

Sample	Total liquid volume (mL)	Oil volume (mL)	Water volume (mL)	Volume % oil	Volume % water	Volume % solids	X	Y	OWR
1.1.1 and 1.1.2	42.5	12,5	30	25	60	15	29	71	0.4
1.4.1 and 1.4.2	41	12	29	24	58	18	29	71	0.4
1.5.1 and 1.5.2	42	14	28	28	56	16	33	67	0.5
1.8.1 and 1.8.2	42	15	27	30	54	16	36	64	0.6

Table 49 Calculation of volume percentage oil, water, and solids contained in the bottom phase of Mongstad sludge treated with MudSplit2

Sample	Total liquid volume (mL)	Oil volume (mL)	Water volume (mL)	Volume % oil	Volume % water	Volume % solids	X	Y	OWR
2.1.1 and 2.1.2	42	12	30	24	60	16	29	71	0.4
2.4.1 and 2.4.2	43	12	31	24	62	14	28	72	0.4
2.5.1 and 2.5.2	42	13	29	26	58	16	31	69	0.4
2.8.1 and 2.8.2	43	15	28	30	56	14	35	65	0.5

