Dewatering of sludge by freezing

Ottavio Franceschini
“Never give in, never give in, never; never; never; never - in nothing, great or small, large or petty - never give in except to convictions of honor and good sense.”

Winston Churchill
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Ottavio Franceschini
Summary
The aim and scope of the project is to study a freezing and thawing apparatus developed by FriGeo AB, company located in Kiruna, in order to enhance the deliquorability of workshop sludges collected from the airport of Arlanda, Stockholm, and other minor sources. Two sludges with different initial characteristics have been analysed. The first sludge (S1) had the following composition: 60 wt% water content, 28 wt% organic matter (oil plus organic substances), and 12 wt% inorganic material (principally fine-grained material). The second sludge (S2) underwent to different pre-treatments to remove part of its water and oil content: 35 wt% water content, 11 wt% organic matter and 54 wt% inorganic material (principally coarse-grained material). Despite the different inorganic composition, the fine-grained material of both the sludges had a similar grain size distribution. The principal internal characteristics and external conditions that influence the dewatering and consolidation of sludges and soils when frozen and thawed have been researched in literature; sludges consolidation is principally enhanced by slow freezing rate (obtained with indirect freezing method at low temperature): while the ice front is moving, the sludge particles are compacted and the oil droplets coalesce, resulting in higher deliquorability while thawing. This effect becomes negligible with high concentration of dissolved substances, salts and impurities. The compaction of soils depends principally on their grain size distribution: three freezing/thawing cycles allow the fine-grained material to reach its maximum compaction; impurities, fast freezing and fast thawing rate contrast this effect. The most suitable parameters among freezing temperature and number of freezing cycles have been chosen varying their values, with the aim to obtain the best deliquorability degree. Soil tubes containing 300 ml of sludge have been placed into a laboratory freezer: 1, 3 or 5 freezing cycles at 5, 10, 20 and 28°C have been performed; the freezing time and the thawing time have been set at 24 hours. Every “24 hours” frozen sample have been let thawed over a 1 mm sieve; after 24 hours, moisture and organic content of the retained material are analysed to evaluate the differences in deliquorability achieved with different freezing parameters. The variation in freezing temperature doesn’t let to a significant change in dewaterability. The first sludge treated with one freezing cycle loses, in average, 60% of its initial water after 24 hours of leaching; 65 and 68% if treated with 3 and 5 freezing cycles, respectively. The second sludge treated with one freezing cycle loses, in average, 33% of its initial water after 24 hours of leaching; 35.4% if treated with 3 freezing cycles. Very little oil flowed away from every sludge sample; indeed the organic content resulted unaltered. The final product is a solid soil like material. The main conclusion from the project is that workshop sludge acts similarly to a soil: the increase of freezing cycles alters the fine-grained material skeleton, resulting in higher compaction and dewaterability, but the differences between one or three freezing cycles is negligible; furthermore, the use of an elevated number of freezing cycles is not viable. The most efficient parameters for the apparatus are one freezing cycle and –10°C. Future developments are needed, especially a cost analysis and a comparison between the results obtained with the freezing apparatus and the results obtained with traditional mechanical and chemical sludge dewatering systems.
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INTRODUCTION
Chapter 1: Introduction

Dewatering sludges is probably the most costly and onerous task on any effluent treatment plant. Most often, sludge must be collected and processed by a waste management company or delivered to a specialized designated hazardous waste site. Typically, these are very expensive options. Moreover, the original producer of such wet waste can be liable for any environmental contamination resulting from improper disposal or handling by an independent contractor. The enormous variety of produced sludges let to an equal amount of suited solutions. Filter presses, belt presses, decanter centrifuges etc. each has their merits and drawbacks, but can be suited to different uses. The choice of the best option for a particular sludge has always to be preceded by an accurate study on that sludge. Wastewater activated sludges and chemical (alum) sludges have been accurately studied during the past years, while it is only in these decades that the study of oily sludges, by-products of petrochemical plants, has begun, with the aim of water and oil reduction. On the other hand, there is a complete lack of studies regarding many other types of sludges. FriGeo AB, Swedish company offering an innovative method for remediation and dewatering based on freezing technology, commissioned for this essay the study of two different kinds of workshop sludges, with the overall goal to figure out, on an experimental basis, the best degree of dewatering and consolidation that they can reach if subjected to freezing and thawing. The evaluation is done varying freezing temperature and freezing and thawing cycles. The essay falls into three main chapters:

- a general overview of sludge and soil freezing is given in the “Literature review” chapter; useful information have been added to make easier for the reader the comprehension of the essay and to help the author in the conduction of the experiments: following this line of thought, the chapter contains an overall description of the composition of sludge and soil and a general introduction to the freezing and thawing technologies applied in several engineering fields. Moreover, a review of the behaviour of soil and sludge while freezing has been added, focusing on the external conditions and internal characteristics of the material that can influence this behaviour. Scientific articles and engineering books have been used;
- on the basis of the read articles, several experiments were thought to characterize the untreated sludge in order to have a comparison with the treated sludges, analysed as well. The “Materials and methods” chapter contains the implemented procedures of the most appropriate experiments;
- the results and the relative discussions have been recorded in the chapter “Results and discussion”; the dissertation has followed in parallel the results, which have prompted several times an upgrade of the literature review and of the experiments.

Evaluation of the results shows that the workshop sludges have a behaviour similar to that of a soil when frozen and thawed; compaction and dewaterability are mainly function of the grain size distribution of the material instead of being related to the freezing temperature. The compaction of the treated material results slightly increased with higher number of freezing/thawing cycles. The alterations in dewaterability due to the presence of oil are not well known yet.
LITERATURE REVIEW
Chapter 2: Literature review

The principal problem regarding sludges (residual semi-solid material left from industrial or wastewater treatment processes, contaminated sediments...) is their disposal in landfills or their reuse in agriculture: the high level of dehydration that the sludge has to achieve can be a costly problem for the treatment plant. Sludge conditioning and dewatering have been extensively studied during these years; the major goal of these treatments is to achieve the maximum dry solid concentration in the dewatered sludge. Unfortunately most of these methods (principally mechanical methods) are limited in the sense that they just remove free water from the sludge, without influencing the bond water that, at the end of the treatment, may still be considerable.

Sludges are composed of particles that are aggregated in flocs, suspended in an aqueous environment or in contact in a solid matrix. Water exists in sludge in different forms; the classification given by Vesilind and Martel (1990) will be used in this study. “Free” water is not associated with the sludge flocs and is free to move within them; free water is easily removed with the conventional mechanical dewatering systems. The water that is trapped inside a floc or is held by capillary forces is called “interstitial” water; a mechanical dewatering device can break the flocs and free the interstitial water. “Surface” water is associated with the single particle by superficial forces. Mechanical systems (like belt filter press or dewatering centrifuge...) can easily remove free water, interstitial water and can hardly remove superficial water. The fourth type of water can be released from the particles only with a thermo-chemical treatment and is called “bond” water (chemically bounded to the particles). In Figure 2.1 the four types of water are shown.

![Figure 2.1: Postulated water distribution in sludge, Vesilind and Martel (1990)](image)

Inorganic (lime and ferric salt) or organic (polymers) conditioners can be used in order to improve the solid content of waste sludge, as emphasized in many studies. However, also the freeze/thaw treatment has been investigated for several years: this treatment is a promising technique that can be used for the conditioning of sludge, enhancing its dewatering characteristics without the use of polymers. The effects of freeze/thaw conditioning are well documented in the literature: many authors have studied this treatment, varying the type of sludge (principally alum sludge, waste activated sludge) and the external freezing configurations (freezing and thawing temperature, freezing rate and direction...), in order to analyse and improve the sludge dewaterability (usually measured as sludge settleability, filterability and floc sizes). All the performed experiments have shown how freezing
influences the sludge flocs both physically and chemically: size, shape and density of the flocs and the bond water content are varied while the ice front advances in the sludge. Freeze/thaw conditioning is able to transform the bond water into free water that can be easily removed by a mechanical method.

Studied by Lazar et al (1999), oily sludges, frequently produced in oil production or processing sites, contain different concentrations of waste oil (40% – 60%), wastewater (30% – 90%), and mineral particles (5% – 40%). The oil can be the continuous phase although the water is in a high percentage. Oil droplets are adsorbed onto solid particles creating a protective layer and the presence of surfactants is the cause of the formation of emulsions. For this, oil creates difficulties in the waste treatment processes and subsequently in the dewatering process. Demulsification treatments are necessary in order to enhance the deliquorability of sludge, reduce its volume, save resources and prevent environmental pollution. Conventional demulsification techniques include electrical, chemical, thermal, acoustic and mechanical methods (Devulapalli and Jones, 1999; He and Chen, 2002). In general, oily sludge is resistant to mechanical deliquoring (Zall et al, 1987; Albertson et al, 1991). The freeze/thaw technique can be used also in the oily sludges treatment. Recent studies (Jean et al, 1999; Jean et al, 2001a; Jean et al, 2001b, Chen and He, 2003; Lin et al, 2008; Yang et al, 2008) have described the efficiency of the freeze/thaw technique in separating the oily phase from the sludge body.

Some kind of sludges can have a composition and a behaviour that are similar to those of a soil; for this reason a quick description of the soil freezing mechanism will be given. The objectives of sludge dewatering and soil preparation for construction are different: in sludge dewatering the water-solid separation is promoted, while the scope of the latter is to obtain a soil non-susceptible to water/solid separation. A soil is a heterogeneous media composed of solid particles, water and air. As shown in Figure 2.2, a frozen soil is a four-phase system: it consists of gases, unfrozen water (film layer of water that surrounds the mineral particles), ice and solid particles. Sludges have higher water content than a soil, for this reason it is more convenient to refer to saturated soils deprived of gases. To describe the composition of a soil in engineering terms the volumetric and the gravimetric fractions can be used as well. The solid particles of the soil, unlike the solid particles of wastewater treatment sludge, are principally composed of small grains of different minerals; fragments of organic matters can also be contained. Soil freezing and prevention of frost heave have been extensively studied, since frost heave can damage the structures built by men, like highways. The freezing of soil can have also a role in civil/mining and environmental engineering purposes: in this case it is more common to use the term “Artificial Ground Freezing” (AGF).
2.1. Direct and indirect freezing

Initially stated by the food engineering, the freeze/thaw treatments can be subdivided into two big categories, according to the kind of contact that the sludge has with the coolant: direct freezing systems and indirect freezing systems. The direct freezing system brings a refrigeration medium into direct contact with the maximum sample surface area, as shown in Figure 2.3a; the barriers to heat transfer are reduced to a minimum. Low temperature gases as well as liquid refrigerants may be used to perform this freezing method. The second technology utilizes a heat transfer surface between the sludge and the refrigerant; as illustrated in Figure 2.3b the sample is separated from the refrigerant by some sort of barrier; these barriers can be sample containers as well as structural components of the freezing systems (Heldman and Lund, 2007).
2.2. Sludge freezing technologies

A second categorization can be made according to the mechanical operation. *Martel et al. (1996)* describes in detail this subdivision, bringing also sketches of the devices. A typical indirect freezing system is the “bulk freezer” (see Figure 2.4a): the sludge is pumped into a tank; a refrigerator is circulated inside the walls of the tank, cooling down its surfaces and freezing the sludge. Thawing is performed in the same tank; meltwater and conditioned sludge are separated. When the tank is emptied a new cycle of freezing/thawing can be performed. Unfortunately, the forces against the tank walls generated by the expansion of ice make this device inclined to rupture after few cycles. A “crystallizer” (Figure 2.4b) uses a direct freezing technique in the conditioning of sludge. A gaseous refrigerant (butane, Freon...) is injected inside the stirred sludge contained in a tank. The resulting slurry of ice crystals and solids is then separated. Like the bulk freezer, a “layer freezer” (Figure 2.4c) is an indirect freezing device: a refrigerated plate is used instead of the tank, avoiding wall stresses. Freezing in thin layers is more efficient, but a large surface is needed.

![Figure 2.4: Conceptual sketches of three sludge freezing devices, Martel et al. (1996)](image)

*Martel et al. (1996)* proposed also a concept for a new freezing device: the “freeze separator” (see Figure 2.5), a combination of a vacuum drum filter with a horizontal belt freezer. The vacuum belt eliminates part of the sludge free water, forming a uniform thin layer of “pre-conditioned” sludge. The pre-conditioned sludge is then completely frozen in the freezing chamber and broken into chunks on a heated roller; the chunks are collected and thawed in order to divide water from solids. Several tests indicate that the proposed freeze separator is technically and economically feasible. With a vacuum level of 100 mm of Hg and a 5.0 minutes of filtration time (optimum operational conditions) the total solid content of alum sludge is increased of 6% (67% of sludge volume reduction); after freezing, thawing
and draining, the remaining granular material had approximately 12% solids; after drying the solid content reached 70%.

The freeze/thaw conditioning method can be applied using either mechanical (as explained before) or natural freezing methods. In cold climate, freeze/thaw conditioning of sludge can be easily and inexpensively accomplished during the winter months outdoor, especially for those small treatment plants that cannot afford to acquire expensive pieces of equipment; an alternative could be transport the sludge into a more specialized central plant, but the relative cost of personnel, equipment and fuel can be expensive. Natural freeze/thaw can effectively dewater sludges from water and wastewater treatment facilities but cannot be accomplished in warm climates for obvious reasons; in these situations, a mechanical freezing device is needed. Martel (1989) developed and designed a new unit operation utilizing natural freeze/thaw for sludge dewatering, called “sludge freezing bed” (see Figure 2.6). The sludge is applied in several thin layers over the bed; each layer is applied as soon as the previous layer has frozen; the bed is covered to prevent snow accumulation and rewetting of the thawed sludge. The sludge freezing bed can be used as the sole method of dewatering or in combination with drying beds to have dewatering of sludge also during the summer months.
A new technology based on the freezing and thawing method is now tested by FriGeo AB in the recycling station of RagnSells, Stockholm. The untreated sludge is placed into a long basin with walls in which circulates the coolant and that allow the sludge to freeze at temperatures between -5 and -30°C; the freezing take place laterally. The basin can be used also as a sedimentation tank prior freezing, to remove part of the supernatant water. When totally frozen, the solid sludge is extracted and let thawed outside, over the ground or over a bed of compost. This kind of technology can be used for different kind of sludges. Figure 2.7 gives a sketch of this new technology.

![FriGeo freezing apparatus](image)

**Figure 2.7: FriGeo freezing apparatus**

### 2.3. Artificial Ground Freezing

Artificial Ground Freezing (AGF) (or Construction Ground Freezing as known in North America) has been first applied in South Wales; it has many applications in civil engineering (see Figure 2.8):

- eliminate the need for structural shoring systems and dewatering;
- create a hard, durable surface for construction equipment, even in soft soils;
- provide a strong, stable support for existing or new foundations near excavations;
- create strong points in the slope for stabilization in landslide mitigation, allowing ground water to flow.
The principle of ground freezing is quite simple and it has never been changed since its first use: the heat is removed from the ground by driving freezing pipes (in which a refrigerant liquid circulates) into it, until the temperature is below the freezing point of the groundwater system; at this point it is possible to start the construction operation. This method can be applied in small scale situations up to great works, like excavations of 45 m diameter and 900 m of depth (*Harris, 1995*).
2.4. Actual applications in environmental engineering

In this paragraph an overview of the freeze technology used in different environmental engineering sectors is discussed. As already cited, the freeze technology, combined with thawing, is an effective method to condition sludges derived from municipal, industrial or petrochemical treatment plants: dewaterability and phase separation is easily accomplished after the treatment, that can be costly efficient, especially in cold regions, where natural freezing can be applied.

Artificial ground freezing (AGF) is a controllable technology that has many applications in the environmental engineering, for example:

- provide an in-situ barrier for containment of contaminated groundwater and a bottom barrier at landfills or other contaminated sites;
- provide temporary shoring for construction of permeable barriers or excavation of contamination;
- create a dry, safe environment for construction and excavation;
- bond soil and waste together to prevent dangerous mixing during removal;
- help with safe retrieval of unexploded ordnance;
- uptake of underwater contaminated sediments and rescue of submerged objects.

The freeze/thaw technology can be applied also to desalinate salt water. Desalination has now been practiced on a large scale for more than 50 years. During this time continual improvements have been made, and the major technologies are now remarkably efficient, reliable, and inexpensive. Water shortage is affecting several countries and its effect is constantly increasing. For this reason the improvement of desalination technologies and the creation of new ones are compulsory. There are three basic approaches with which it is possible to perform the desalination:

1. change the phase of the water and use a physical method to separate the salt from it;
2. physical separation of the components (usually with a membrane) through an externally applied gradient;
3. chemical approaches.

In this optic, the freeze/thaw approach falls into the first category. Direct, indirect and natural freeze processes can be applied: in a direct freezing process, the refrigerant is mixed directly with the brine; in an indirect process, the refrigerant is separated from the brine by a heat transfer surface. A schematic of an indirect process is shown in Figure 2.9. The process is essentially a conventional compressor that drives refrigeration cycles. There are several schemes to separate the ice from the brine, like centrifuging or flowing the slush upward in a column. The brine is then drawn off through peripheral discharge screens. A counter current flow of freshwater is fed into the top of the column to wash any remaining brine from the ice. The washing can be accomplished with the loss of only a few percent of the freshwater product. The ice is then fed to the melter where freshwater is recovered. A heat exchanger is used to recover energy from the freshwater and reject brine by precooking the feed (Spiegler and El-Sayed, 1994).
Due to the physical contact between refrigerant and water and the possibility of a contamination, the direct freezing desalination methods have never been used on large scale. The natural desalination employs the naturally occurring freeze/thaw cycle of the winter months to desalt water; the resulting product can have later application in agriculture or for other water supplies. A recent study that applies this approach to saline groundwater in North Dakota showed that this method can be costly competitive with the reverse osmosis method, that is actually the state of art between the desalination technologies (Boyson et al, 1999).

FriGeo AB, in collaboration with Luleå University of Technology, developed an innovative dynamic method to uptake contaminated sediments and objects, called “freezing dredging”. The main idea with the freeze dredging is to stabilize the contaminated sediments by artificial freezing under the water surface and then pick them up while frozen. Brine conducting pipes are arranged in a way that enables freezing, lifting and unloading of the frozen material; the structure is called “freezing-cell”. The brine circulating in the freeze-cells are kept at a temperature of -20 to -40°C, using a mobile freeze plant (Figure 2.10). In order to avoid suspension of the sediments, a lifted frozen cell should be surrounded by other cells. The freezing process alters the collected material: the freeze/thaw cycle improve the dewaterability of the sediments while thawing under drained conditions (Rostmark S. 2004).
2.5. How sludge freezes

Suspensions like activated wastewater sludge, alum sludge, sewage sludge, scum sludge and oily sludge can be well conditioned using the freeze/thaw treatment. Water is a unique substance that expands in volume when it becomes ice; ice is a solid that consists of a crystallographic arrangement of water molecules, where the positive charge concentrations of one molecule are strongly bonded with the negative charge concentrations of another (Glen, 1974). This attraction plays a major role in the organization of the structure of the ice crystals that has a great regularity and symmetry. Because of this highly organized structure, other atoms, molecules or particles cannot become part of the ice crystal lattice without severe local strain and are rejected by the advancing surface of a growing ice crystal. Ice crystals grow by incorporate water molecules only and continue to grow as long as water molecules are available. The solidification front may interact with the particles in three distinct modes depending on the advancing velocity of the front: below a certain value (called “critical velocity”) the front may push the particles indefinitely and segregates them in the last-freezing liquid, or the front may engulf the particles after having pushed them over some distance, or the front may engulf the particles instantaneously upon contact (Lipp and Körber, 1993; Ashtana and Tewari, 1993).

The frozen and thawed flocs of sludge will be named “zots”. This term was first used by Russian researchers (Zolotavin et al., 1960), who recognized that the chemical and physical properties of a frozen/thawed floc were drastically different from an untreated one, and so the warranting to use a separated term. Only flocs that are trapped by the ice front are named zots.

Many authors stated that a necessary prerequisite to obtain an effective improvement in sludge dewaterability is a low freezing rate; the low freezing velocity starts up a freezing mechanism in the sludge sample called “gross-migration”, initially studied by Longsdon and Edgerley (1971). Assuming that a sludge sample is placed upon a cold surface and frozen slowly, the floc particles are not trapped but continuously rejected by the ice front. This mechanism continues till all the particles are pushed in the top and pure or nearly pure ice is below; since ice grows just incorporating water molecules, the solids at the top of the sample are dewatered (see Figure 2.11).

![Figure 2.11: Mechanism of gross migration; A) freezing starts; B) water flow remains good as freezing continues; C) All solids are pushed to the top of the ice. Longsdon and Edgerley, 1971](image)
When the freezing speed is faster, “micromigration” occurs (see Figure 2.12) and most of the particles are trapped in the ice, becoming zots.

As stated by Parker et al. (1996) there are three ranges of freezing front velocities: the first two are discussed above and describe a planar moving interface with or without particles inclusions at a low and medium freezing rate; the floc particles trapped by the ice front are subjected to strains due to the growing columnar ice crystals. At higher freezing rates (greater than 75 mm/h) it has been observed that spikes of ice (called “dendrites”) grow into the unfrozen sludge in the direction of freezing, generally bypassing the sludge flocs, apparently without moving or altering them. Following this primary longitudinal growth, there is a second lateral growth at slower rate with the shape of branches that pushes the particles laterally. As an example, Parker et al. (1998) studied the interaction between flocs and the ice/water interface on alum sludge with a total solid content of 1% varying the freezing rate (velocity of the ice/water interface). To perform these experiments, a Bridgman apparatus has been used: an optical microscope allowed the analysis of the ice front movement and the variation of the freezing rate (approximated by analyzing video footage of the freezing, captured with a CCD camera). With a freezing speed of 25 mm/h (low freezing rate) the interface is planar; the large floc particles are pushed ahead of the interface without physical changes in the structure due to the abundance in free water. With an intermediate freezing rate (25 to 50 mm/h) the ice/water interface advances irregularly and is harder to identify; flocs migrate ahead the front but the rejection is not complete: broken pieces of flocs are incorporated into the ice while the front is moving. Fast freezing rate (200 – 600 mm/h) leads to the formation of dendrites: the flocs are not rejected, but trapped and fragmented.

From microscopic observations on oily sludge from a petroleum refinery plant, Jean et al. (2001)b concluded that, thanks to the freeze/thaw technique, not only the flocs became more compact and much larger, but also that the tiny oil droplets were not as prevalent in the microphotograph of the frozen/thawed sample as they were in the original oily sludge: physical forces associated with the motion of the ice front push the oil droplets together; some oil droplets can be trapped inside the flocs too. The weight fraction of the oily phase was 22.9 wt%; the oily sludge was an oil-in-water (O/W) emulsion.
A demulsification mechanism for water-in-oil (W/O) emulsions has been described by Chen and He (2003). They stated that the film at oil-water interface and the surfactant distributed on it play very important roles for the stability of the emulsion (Figure 2.13(a)); when the temperature decreases and the droplets of water freeze, some of the surfactant molecules are expelled from the ice lattices and can diffuse into the oil phase (Figure 2.13(b)); during thawing, more surfactant molecules diffuse away from the ice because the interface film melts first. The surface tension force pulls the melted water molecules together (Figure 2.13(c)); due to the lack of surfactant on the interfacial film, the water droplets coalesce to form larger water droplets and some surfactants gather together to form micelles inside the water droplets with a trace amount of oil (Figure 2.13(d)). The demulsification is achieved.

Lin et al. (2008) divided the W/O emulsions into two categories, depending on which phase freezes first: OFBW when the oil phase freezes before the water and NOFBW when the oil phase does not freeze as the water droplets do. The two mechanisms of demulsification are slightly different and can be summarized as follow: when the oil freezes, it creates a cage in which the water droplets are trapped (Figure 2.14(b)); this cage is broken due to the expansion of the formed ice; liquid droplets permeate inside the cracks forming a large network, bridging droplets (Figure 2.14(c)). During the thawing phase, the network fuses and the droplets coalesce (Figure 2.14(d)). The phase separation is accomplished by differences in density (Figure 2.14(e)).
2.6. How soil freezes

While freezing, the ice in the soil voids becomes a bonding agent, connecting together soil particles and increasing the soil strength. The freezing process depends principally on the kind of soil: in saturated sand or gravel (non-frost susceptible) the freezing is not necessary associated with a volume expansion of +9%, because part of the water can be expelled during freezing. In a saturated silt or silty sand (often termed “frost susceptible” soils), under slow freezing rate conditions, the crystallization of ice within the larger soil voids (and the subsequent extension) forms continuous ice lenses, layers and veins. An ice lens grows through capillary rise and thickens in the direction of heat transfer until the water supply is depleted or until the freezing conditions at the freezing interface no longer support further crystallization; ice lenses develop only in fine-grained soils. As the ice lens grows, the soil and pavement will “heave” up potentially resulting in a cracked, rough pavement. Under fast freezing rate conditions the water contained between the voids freezes in situ. Figure 2.15 illustrates the formation of ice lenses in a frost susceptible soil under slow freezing rate conditions (Andersland and Ladanyi, 2004). Colbeck (1982), thanks to microscopic investigations, determined how water freezes in an artificial soil matrix: the pore water starts freezing in the middle of the pore, leaving an unfrozen water film in the region closest to the particles.

On thawing the ice disappears and the soil skeleton must adapt to a new equilibrium void ratio, depending principally on the kind of soil that has been subjected to freezing, on the draining conditions and on the thawing rate and temperature.
2.7. Internal characteristics that influence the consolidation of sludge

2.7.1. Water content

Kerosene W/O emulsions with different water content were treated with dry ice by Lin et al. (2007). The emulsion samples of 8 mL (sealed in a plastic tube which is 100 mm in height, 12 mm in outer diameter and 0.5 mm in wall thickness) were frozen in dry ice (-78°C) and subsequently thawed and settled down in ambient air (18 - 20°C) for 10-15 hours. Dewatering ratio resulted about 25% for the sample with 30% water content, while for a water content of 65% the dewatering ratio was higher than 96%. The authors reported that this trend was principally influenced by 2 factors: the increase in water content shortens the water droplet-droplet distance, making easier a collision during freezing; on the other hand the settling rate of the water droplets decreases exponentially with an increase in the droplet fraction (water content), due to the more tortuous route of one droplet between the others.

2.7.2. Organic matter

Örmeci and Vesilind (2001) collected activated sludge (from North Durham Wastewater Treatment Facility) and alum sludge (from Brown Water Treatment Facility, Durham, NC) to investigate the effect of dissolved organic material and ions in the
freeze/thaw conditioning treatment. Sludge samples of 100 mL were placed in 130 mL transparent glass bottles and frozen at -8°C for 36 hours. The thawing was performed at air temperature for 10 hours (it has been recognized that a thawing time longer than 12 h would have started undesired anaerobic reactions in the sludge and changed its characteristics). Dewaterability, settling and supernatant characteristics were measured before and after the treatment (capillary suction time -CST- was not performed because, as stated from other studies, underestimates the dewaterability of sludge), together with ECPs (extracellular polymers), and cation concentration. Protein, carbohydrates and cation concentrations in the sludge supernatant increased remarkably after freeze/thaw conditioning of activated sludge due to the release of ECPs from sludge flocs and intracellular material from disrupted cells (due to the pressure created by the expanding ice). Frozen/thawed alum sludge, initially poor in proteins carbohydrates and cations, didn’t change noticeably in the concentration of these elements, indeed it is mainly composed of inorganic material. The presence of high concentration of dissolved ions and organic material in the activated sludge influences the growing pattern of ice: micromigration occurs in activated sludge reducing its dewaterability. On the other hand, in alum sludge, particles are more easily pushed by the growing ice/water planar interface without being trapped; ice crystals grow in columns as long as the freezing rate is slow enough, allowing a better dewaterability of alum sludge. The removal of dissolved organic material and ions in the activated sludge has improved the effectiveness of the freeze/thaw conditioning: the resulting zots were smaller and denser, resembling the alum sludge zots. The lower the concentration of impurities in the sludge, the better its dewaterability.

2.7.3. Impurities

Halde (1979) studied the differences in concentration in digested sewage sludges with different fractions of dissolved substances (created by dilution). He found that low concentration sewage sludge was readily concentrated. The concentration was affected by the amount of dissolved substances and the particle size distribution of the sludge; raw primary sludge containing a large fraction of coarse particles is a lot easier to concentrate than a digested sludge containing smaller particles and a high amount of solute.

Chu et al (1997) studied the effect of sodium chloride on waste activated sludge collected from the wastewater treatment plant of Neili Bread Plant, Taoyuan, Taiwan. Common analyses have been performed on the sludge: COD, SS, turbidity. Sodium chloride was dissolved into sludge samples to reach a mass percentage equal to 0.5, 1.0 and 2.0 wt%. Tubes containing subsamples of the modified sludges have been immersed into a freezing pool closed in a chamber at a constant temperature at -17°C. Results confirmed that the NaCl retards the gross migration and is unfavorable to effective dewatering.

To study the effect of dissolved solids on alum sludge, Martel (1999) observed the change in ice crystal structure and aggregated particle size as function of NaCl concentration. The alum sludge (chosen due to its low initial concentration of dissolved solids) was collected from the water treatment plant in Lebanon, NH; the initial total solids concentration was 1.4%. After mixing, eight 1 L samples were taken; various amounts of NaCl, ranging from 0 to 2000 mg/L, were added to each sample. Table 2.1 shows the amount of added NaCl to each liter of alum sludge and the corresponding conductivity.
Table 2.1: Amount of added NaCl to each liter of alum sludge and the corresponding conductivity

<table>
<thead>
<tr>
<th>Sample #</th>
<th>NaCl added [mg]</th>
<th>Conductivity [μmho/cm], 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>128</td>
</tr>
<tr>
<td>2</td>
<td>12.5</td>
<td>125</td>
</tr>
<tr>
<td>3</td>
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<td>177</td>
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<tr>
<td>4</td>
<td>50.0</td>
<td>237</td>
</tr>
<tr>
<td>5</td>
<td>75.0</td>
<td>285</td>
</tr>
<tr>
<td>6</td>
<td>100.0</td>
<td>339</td>
</tr>
<tr>
<td>7</td>
<td>500.0</td>
<td>1154</td>
</tr>
<tr>
<td>8</td>
<td>2000.0</td>
<td>3890</td>
</tr>
</tbody>
</table>

300 mL of each sludge sample were poured into small aluminium bread pans and frozen at -18°C. This formed a small frozen sludge cake that was then sliced in slices of 1±2 mm thick. These slices were then mounted on a glass slide and placed on a light table equipped with a crossed polarizer, allowing the recognition of clear ice and solid fraction. Photos of the cross sections revealed two distinct patterns in the way the solids were aggregated: below a concentration of 100 mg/L of NaCl, ice crystals grew by attaching water molecules along a planar front (the ice crystals grow in a columnar shape, the pattern is called “gross migration”) till the flocs are entrapped after rejection; at NaCl concentrations greater than 100 mg/L, the ice crystals grew as a series of parallel plates (the pattern is usually called “micromigration”) and the solids were displaced between them and not ahead of a freezing front. Moreover, the mean grain size decreased as more NaCl was added to the sludge; the filterability should still be high compared to unconditioned sludge. The conductivity of the alum sludge at the transition from the two ice grown patterns ranged from 339 to 1154 μmho/cm, which is typically less than most wastewater sludges: this explains why the aggregated particles in the freeze/thaw conditioned alum sludge are larger than those of waste activated sludge (or other sludges in general) and explains the differences in dewaterability. This study shows that micromigration is favoured not only by a fast freezing rate, but also by the concentration of dissolved solids.

2.7.4. Oil content

Jean et al. (2001)b analysed different types of sludges with different oil contents, sampled in the wastewater treatment plant of the Chinese Petroleum Corp, Taoyuan, Taiwan. Samples of scum sludge (weight fraction of the oily phase estimated to 22.9 wt%), waste activated sludge (weight fraction of the oily phase estimated to 0.16 wt%) and tank residual sludge (weight fraction of the oily phase estimated to 98 wt%) were put in containers of radius 2.3 cm and height of 4 cm and then placed in a -16.5°C room for 24 hours (the curing effect proposed by Parker et al. (1998) was not considered). The freeze/thaw treatment markedly enhanced the deliquoring rate of the scum sludge: the time required for deliquoring was reduced from 3000 s to less than 200 s. Deliquoring the activated sludge is easier: from 700 s to deliquoring the original activated sludge to less than 50 s after the treatment. Freezing and thawing don’t affect the tank sludge, due to its high viscosity and the presence of heavy hydrocarbons in the residual.

2.7.5. Kind of oil phase

Lin et al. (2008) prepared 9 kinds of model W/O emulsions with various oil phases (cyclo-C6, n-C6, n-C7, n-C8, n-C9, n-C10, n-C12, n-C14 and kerosene) and with the same phase
Chapter 2: Literature review

of 1.0 M NaCl aqueous solution. Emulsion samples of 8 mL (sealed in plastic tubes of 100 mm height, 12 mm in diameter and 0.5 mm in wall thickness) were frozen in a freezer (-35°C, 24 h), cryogenic bath (-45 and -60°C, 1.5 h), dry ice (-78°C, 1.5 h), and liquid nitrogen (L-N2, -196°C, 1.5 h), respectively, and then thawed in ambient air (16 to 18°C) for 10-15 h. The results showed that no emulsions were demulsified at -35 °C, but in the temperature range from -45 to -196 °C, two different tendencies of the dewatering ratio as a function of freezing temperature were observed. For the four emulsions prepared with cyclo-C6, n-C14, n-C12, and n-C10 as the oil phase, (first emulsion group), their dewatering ratios dramatically increased with the decrease in the freezing temperature (-45 to -60°C) and then increased slightly or levelled off. The ratios were over 85% at -60°C and reached nearly 100% at -196°C. However, the remaining five emulsions (second emulsion group) were relatively hard to break and were very sensitive to freezing conditions. Their dewatering ratios reached a peak of 70% in the range from -45 to -78°C, whereas no water was separated by L-N2 freezing. All the differences in the demulsification performances between the two groups depend on the physical properties of the oil phases (freezing point, specific heat capacity, thermal conductivity, density and viscosity); the principal difference between this two groups has been found to be the freezing point: the first group has a much higher freezing point than the second group. It has been possible to conclude that when the oil phase freezes before the water droplet phase does (OFBW), the emulsion (first group) is demulsified readily, but when the oil phase does not freeze as the water droplet phase does (NOFBW), the emulsion (second group) is relatively hard to break. Similar behaviours were found using NH4Cl, NH4NO3, KNO3 and NaNO3 aqueous solutions instead of NaCl aqueous solution.

2.7.6. Water droplet size in W/O emulsions

Lin et al. (2007) showed how the dewatering ratio of W/O kerosene emulsions with the same water content of 60% changes with different water droplet sizes. The emulsion samples of 8 mL (sealed in a plastic tube which is 100 mm in height, 12 mm in outer diameter and 0.5 mm in wall thickness) were frozen in dry ice (-78°C) and subsequently thawed and settled down in ambient air (18-20°C) for 10-15 h. The mean water droplet sizes varied from 2.7 to 10.1 μm. The lowest dewatering ratio of 74% was obtained in the emulsion with the smallest droplets size (2.7 μm); as the droplet size increased, the dewatering ratio increased, reaching 95% for droplet sizes of 7.3 and 10.1 μm.

2.8. External conditions that influence the consolidation of sludge

2.8.1. Variation of freezing time at same temperature

Vesilind and Martel (1990) investigated the effect of freezing time on concentrated waste-activated sludge and raw primary sludge. The results showed that the freezing time for an activated sludge has a marked effect on its subsequent dewaterability: the longer time allows the difficult-to-freeze bond water to become part of the ice crystal and the particles to attach themselves to each other (Figure 2.16).
Chen and He (2003) studied the effect of water content and freezing time on oily sludge generated from the pre-treatment step of the used lubricating oil re-refinery. The oily sludge was a tight water-in-oil (W/O) emulsion with oil as continuous phase. Eight emulsions with different water contents were prepared, as shown in Table 2.2; 9 g of each emulsion were filled in 15 mL tubes. A constant freezing temperature of -40°C was applied. Ten samples of each emulsion were placed into the freezer at time zero; one sample of each emulsion was extracted at a particular time and thawed at 19°C. The results (Figure 2.17) showed that in order to obtain a plateau value of dewatering ratio, 6 h of freezing are necessary (except #7). This time is necessary to completely freeze the water phase and expel the surfactant molecules.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content (wt.%)</td>
<td>38.7</td>
<td>39.3</td>
<td>40.0</td>
<td>42.4</td>
<td>43.8</td>
<td>57.9</td>
<td>76.3</td>
<td>77.0</td>
</tr>
</tbody>
</table>

Table 2.2: Initial water content of the oily sludge
2.8.2. Variation of freezing/thawing cycles

No literature has been found for what concern the effect of freezing and thawing cycles on the compaction and dewaterability of sludge.

2.8.3. Variation of curing time

*Chen et al. (2001)* investigated the effect of curing time on “high speed” frozen sludge. The treated samples were waste activated sludge and alum sludge. LN₂-freezing was achieved using plastic containers of radius 4.25 cm and height 5.0 cm, containing sludge samples; the containers were then immersed in the LN₂ pool at -196°C for 3 min. The average freezing speed was estimated to be 200 μm/s. Some samples were cured in the LN₂ pool for 2–24 h; others were cured in a freezer at -20°C for 2–24 h. Some untreated sludge samples were directly placed in the -20°C freezer for 2–24 h (without LN₂ freezing) and cured for 0–22 h for comparison. The results showed that:

- The high-speed freezing using LN₂ does not affect the dewaterability of alum sludge: CST is reduced from 117 to 50 s; the bond moisture content is reduced; the ZSV (settleability) is increased from 50 to 70 μm/s.
- The high-speed freezing using LN₂ has a negligible effect on the activated sludge: ZSV and bond moisture content remained unchanged; only CST is slightly affected.
- The slow freezing rate exhibits the greatest improvement in dewaterability, including filterability (much less CST), settleability (greater ZSV), and bound moisture content.
- Curing has no effect with high-speed freezing (LN₂-freezing) but significantly enhances the sludge dewaterability with slow freezing.
- After LN₂-freezing, the floc size of alum sludge decreases: the growing fingering ice front (dendrites) fragments the original sludge flocs; the change in floc size for activated sludge is negligible.

Moreover, the authors stated that “ultra-rapid” freezing cannot condition the sludge: the vitrification of water would not alter the structure of the sludge flocs because no ice crystal could nucleate or grow.

2.8.4. Variation of freezing rate and temperature

To verify their sludge freezing model, *Vesilind and Martel (1990)* studied the effects of freezing rate and final temperature using samples of a concentrated waste-activated sludge and raw primary sludge. To investigate the effect of the final freezing temperature, four samples of 250 mL have been frozen at -6°C for 24 hours and then moved in colder boxes for 24 additional hours; the freezing rate is the same, but the final temperature is different. The samples were then thawed at air temperature for 24 h; the results showed an increase in filterability with a decrease of the final freezing temperature for both sludges, due to the pressure between particles at low temperatures (Figure 2.18a). The effect of freezing rate has been investigated by placing the sludge samples in four different cold boxes and freezing them at different rates for 24 h. After being thawed at air temperature for 24 h, the results showed that the best dewaterability occurs when the sludge freezes in the least cold environment and the freezing rate is the slowest. The results are shown in Figure 2.18b. The
authors concluded that the freezing rate is the principal governing variable that determines the dewaterability of frozen/thawed sludge.

A fast freeze/thaw treatment on excess activated sludge taken from the wastewater treatment plant in Hsinpu Fiber Plant, Hsinchu, Taiwan, was studied by Lee and Hsu (1994); prior characterization analyses were performed. For this study a series of PP plastic bottles of 12 cm in both diameter and height were filled with sludge and immersed in a water/ethylene-glycol pool at -15°C. The time needed to freeze completely the sample was about 1.5 h with an average freezing speed of 40 mm/h (11 μm/s) to be referred as “fast” freezing velocity. The thawing phase was performed at room temperature for 18 h. Drying tests, centrifugal settling tests and vacuum filtration tests were performed in order to demonstrate the effect of the fast freeze/thaw treatment on the sludge dewaterability. After treatment there has been a significant increment in both BOD and COD values of the supernatant; the moisture movement resistance and the bound water content of the sludge cake both decrease, the floc volume and the sludge compressibility are reduced, and the sludge filterability is improved greatly.

In order to verify the applicability of their freezing device (see Figure 2.5), Martel et al. (1996) performed different freezing tests on alum sludge with different freezing temperatures: -5, -14, -23, and -30°C. Three samples with different total solids contents were prepared, in order to simulate the characteristics of the sludge at every step of the device process. A solid content of 2% represents a typical alum sludge after gravity thickening; a 6% solids content represents a typical alum sludge after vacuum filtration; a 12% solids content simulate a typical alum sludge after dewatering with a conventional belt press. To simulate layer freezing, the sludge was frozen in layers 6 mm thick. Results showed that the effective grain size ($D_{10}$) decreases as the freezing rate increases and that a higher initial solid content produces larger grains. To test the influence of curing time, samples containing 2% of solids...
were frozen and then cured at -4°C for 1 and 24 h. No effects on the grain size were observed with the variation of curing time.

Tests regarding the effect of the freezing velocity on the sludge compaction were performed by Hung et al. (1996). In the experiments, a waste-activated sludge from Neili Bread Plant, Taiwan, had been used. The sludge was placed in glass tubes of 1.3 cm diameter and 15.0 cm height and then frozen with a freezing speed that ranges from 1.41 to 72.6 μm/s. The results show that, in order to improve the sludge settleability and reduce the bond-water content to improve filterability, the freezing speed should be less than a critical value (3 μm/s in this study); the change in sludge characteristics after the freeze/thaw treatment is caused primarily by the modification of the floc structure, which is more compacted due to the squeezing action of the ice crystal growth. When the freezing velocity surpassed the value of 22 μm/s no gross migration occurred. These values are strongly influenced by the particle size, surface properties and presence of dissolved impurities.

Parker and Collins (1998) tested capillary suction time, filterability, cake solid content, settleability and aggregate volume index on alum residual with initial total solid (TS) contents equal to 1, 3, 5 and 10%, before and after directional freezing in a liquid nitrogen bath (-196°C). The samples volume was 250 mL, contained in an aluminium pan (15 cm diameter), resulting in 1.4 cm of sludge depth. The samples were frozen for 2 min (ultra-rapid rate) and then cured at -10°C for 0, 1, 6 or 24 h. Ultra-rapid freezing rate produces zots that are smaller and with slower settleability than those produced using a slow freezing rate; however ultra-rapid freezing still leads to significant improvement in dewaterability. Moreover, ultra-rapid freezing of the unthickened residuals created zots that were smaller than the original flocs: flocs are incorporated singly, not as agglomerates, and are fragmented by the dendrites; and shrunk once entrapped due to dehydration. Curing time improves the dewaterability characteristics of the frozen sludge, although 24 h of curing do not appear to yield better results than a curing time of 6 h.

Jean et al. (1999) tried for the first time to apply the freeze/thaw technique to an oily sludge taken from a DAF (dissolved air flotation) unit of wastewater treatment plant located in Chinese Petroleum Co., Taiwan. The weight fraction of oil was 22.9 wt%, the residual solid content was 7.8 wt%. The sludge samples were put in glass tubes of 1 cm diameter and 15 cm height. Those that were immersed in a freezing pool at -20°C for 24 hours (without considering the curing effect (Parker et al., 1998; Hung et al., 1997)) and thawed under room temperature for 12 hours showed a separation of phases in layers with an increase in filterability and settleability; the capillary suction time (CST) was decreased from 201 s to 26.8 s and more than 50% of the oil content existing in the original sludge had been separated. To illustrate the effect of freezing speed, some samples were immersed in saturated liquid nitrogen (-198°C) for 30 min (ultra-fast freezing with a freezing rate that exceeds 50 K/s) and then thawed at room temperature for 12 h: the CST resulted in 112 s, but no phase separation occurred.

Jean et al. (2001) found that ultra-fast N₂ freezing only slightly affected dewaterability for activated sludge and sewage sludge. The dewaterability of ferric hydroxide sludge is improved by using an ultra-fast rate, while it is not beneficial for oil separation or for filterability enhancement in oily sludge.
Chen and He (2003) studied the effect of water content and freezing temperature on oily sludge generated from the pre-treatment step of the used lubricating oil re-refinery. The oily sludge was a tight water-in-oil (W/O) emulsion with oil being the continuous phase. Eight emulsions with different water contents were prepared, as shown in Table 2.2; 9 g of each emulsion were filled in 15 mL tubes. The first seven samples were frozen at different temperatures: -13, -21, -40 and -55°C for 29 h. Thawing was carried out at 19°C in ambient air. The dewatering rate results are shown in Figure 2.19: the dewatering ratio for the high water content ratios are between 75 and 95%. For those samples with water content less than 50% the dewatering ratio increases with the decrease of the freezing temperature and reaches a level of about 60% at -40°C, then the dewatering ratio decreases to below 20% at -55°C. It was possible to conclude that the higher the water content (larger droplets) in the emulsion, the higher the starting freezing point; lower water content makes difficult the demulsification of an oily sludge.

![Figure 2.19: Effect of freezing temperature; Chen and He (2003)](image)

Lin et al. (2007) froze a kerosene W/O emulsion at a series of temperatures from 0 to -60°C; the solidification of the droplets phase was achieved at -27.5°C. A cryogenic bath was used to freeze the samples. Demulsification didn’t occur at 0°C; when the freezing temperature was lower than the solidification temperature, the demulsification performance was obviously increased. Dewatering ratio was 86% at -30°C and surpassed 90% at -38, -45 and -60°C. The authors performed the same experiment using a refrigerator instead of a cryogenic bath: the results showed that, when frozen in a cryogenic bath, all the dewatering ratios were about 90%, while they were from 59 to 70% when frozen in a refrigerator. In a refrigerator the cold air freezes the droplets really slowly (slow rate), limiting the strains against the frozen oily phase. In the cryogenic bath, the crystallization in the emulsion develops at a relative fast rate. The relative fast crystallization enhances the strength of droplet collision and then ruptures the oil film easily. An ultra-fast cooling rate (-196°C) was not suitable for the demulsification of the emulsion.

2.8.5. Variation of freezing direction

Directional solidification is used to study sludge freezing for two reasons. First, it allows incorporation and rejection to be quantified. Second, it simulates natural freezing and most commercial ice-making processes (Parker et al, 1998).
Hung et al. (1997) used a vertical freezing apparatus and a radial freezing apparatus on waste activated sludge samples to compare floc characteristics and the associated composition changes. In the “radial freezing” the ice front develops in the sludge samples from the rim region toward the central region along the radial direction. The samples were frozen at -20°C in the respective apparatus. The results showed that the degree of gross migration versus freezing speed was similar for both vertical freezing and radial freezing conditioned sludge; the floc characteristics after radial freezing are slightly different than those after vertical freezing; shape, filterability, settleability, floc density versus size, chemical composition and interstitial water content are similar in both the freezing direction. Concluding, it is the freezing speed itself (or more precisely, the corresponding gross floc migration) that principally influences the sludge dewaterability, and not the freezing direction.

2.8.6. Variation of thawing rate and temperature

Chen and He (2003) studied the effect of water content, thawing rate and temperature on oily sludge generated from the pre-treatment step of the used lubricating oil re-refinery. The oily sludge was a tight water-in-oil (W/O) emulsion with oil being the continuous phase. Eight emulsions with different water contents were prepared, as shown in Table 2.2; 9 g of each emulsion were filled in 15 mL tubes and frozen at -40°C for 40 h. To analyse the effect of the thawing rate, the samples were thawed at 19°C for 45 min in water bath and in ambient air. Results are shown in Table 2.3. When the thawing rate is slow (ambient air), the time that allows the surfactant to migrate away from the interface ice/oil is longer and thus more water can be removed. At high water contents the effect of the thawing temperature is not so remarkable.

<table>
<thead>
<tr>
<th>Sample#</th>
<th>1</th>
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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
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<tbody>
<tr>
<td>Water content (%)</td>
<td>38.73</td>
<td>39.29</td>
<td>39.77</td>
<td>42.35</td>
<td>43.75</td>
<td>57.86</td>
<td>76.32</td>
</tr>
<tr>
<td>In water (fast thawing rate)</td>
<td>61.57</td>
<td>51.05</td>
<td>13.40</td>
<td>50.41</td>
<td>36.59</td>
<td>82.51</td>
<td>84.82</td>
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<tr>
<td>In air (slow thawing rate)</td>
<td>69.46</td>
<td>61.91</td>
<td>70.92</td>
<td>66.58</td>
<td>53.65</td>
<td>76.81</td>
<td>82.65</td>
</tr>
</tbody>
</table>

Table 2.3: Dewatering ratio thawed completely at 19°C in water and in air (%)

Figure 2.20 shows the results of thawing all the samples in water bath at different temperatures for 1 h: for low water content samples, thaw at 10 °C can remove about 70% of water from the emulsion while less than 40% of water can be removed if thawed at temperatures higher than 50 °C.
Yang et al. (2008) studied the differences in the demulsification rate of a model emulsion (dodecane, 30 %v/v deionized water, 3 to 9 g/L of asphaltenes and 0.47 to 3.3 g/L of resins) with the freezing/thawing treatment using three different thawing methods: air temperature (20°C), water bath (40°C) and microwave oven (700W, 2450 MHz). The samples (10 mL) were previously frozen in a refrigerator at -25°C for 20 h. The results showed that the emulsion stability is affected largely by the concentration of the asphaltenes or resins. At every concentration of asphaltenes, the dehydrating ratios obtained when thawing with microwave irradiation were always higher than those obtained with the other thawing methods (Figure 2.21).

2.8.7. Variation of freezing method

Knocke and Treherne (1988) tried direct and indirect freezing methods on chemical and biological sludges. In the indirect freezing method the sludge samples (1 liter) were placed in a commercial freezer at -10°C for 2-4 h; after that time, thawing was performed at room temperature, 20-22°C. For what concern the direct freezing method, sludge was stirred in a freezing chamber in contact with butane or Freon 12 (the schematic of the apparatus is shown in Figure 2.22); specific resistance, particle size distribution, floc density and dry solid
density were analysed on the treated sludges to compare the differences between direct and indirect freeze/thaw conditioning.

- Results show that the indirect freezing method was the only conditioning method which consistently resulted in a marked improvement in the cake solids concentration for alum sludge and, in a lesser extent, waste activated sludge. Rates of dewatering were also markedly improved. After treatment the sludge had a granular appearance, despite its prior “gelatinous” consistency. A significant decrease in fine particles concentration was observed after conditioning with the indirect method, due to their aggregation into larger particles; furthermore the sludge flocs density increased considerably.

- The direct freezing conditioning obtained more variable results and lower benefits over the use of an indirect freezing method; the rate of freezing was relatively rapid, with a detention time lower than 45 min. Either butane or Freon 12 conditioning resulted in a significant increase of fine-size particles (5-10 μm), due to cell rupture.

![Figure 2.22: Schematic of direct freeze conditioning apparatus; Knocke and Trehern (1988)](image)

2.9. Internal characteristics that influence the consolidation of soil

2.9.1. Soil type and particle size

As stated before, a frost-susceptible soil defines its behaviour in frost heaving and in thaw weakening. As illustrated in Figure 2.23 the range of possible degrees of frost susceptibility (on the ordinate, from negligible to very high) is wide for most of the soils, but in general it is possible to refer a sand/gravel soil as non-frost susceptible and a silty soil as frost susceptible.
2.9.2. Polluting agents

Ladanyi (1989) demonstrated that an increased salinity can reduce the ice content in the soil and a consequent reduction in the frozen soil strength. The presence of salts in the pore water increases the freezing-point depression, increases the unfrozen water content and reduces the soil frost-susceptibility.

Of course also the presence of other polluting agents can influence the thermochemical properties of a soil (freezing temperature, unfrozen water content), making more
complicated its freezing behaviour (Frèmond, 1994). The presence of these polluting agents, consequently, influences also the compaction of the soil that has undergone thawing.

2.10. **External conditions that influence the consolidation of soil**

2.10.1. Freezing and thawing rate

As cited before, the effect of freezing in a saturated silty soil depends principally on its freezing rate: a fast freezing rate will make the water contained in the voids to freeze in situ, while with a slow freezing rate there will be the formation of ice lenses and a consequent frost heave. In presence of free capillary water and slow freezing rate, the formation of ice lenses brings a total moisture content in the soil that is greater than the moisture content corresponding to its unfrozen state. In this case, if thawing occurs fast enough, frozen ground will be transformed into a slurry of soil particles and water, because the production of meltwater is faster than the draining rate; on the other hand, a low thawing rate under drained conditions will produce a volume change in the soil and settlement (consolidation) under its own weight; furthermore slow freezing permits local ice segregation and a consequent irreversible soil consolidation. In coarse-grained frozen soils, the consolidation due to thawing is small (Andersland and Ladanyi, 2004).

2.10.2. Freezing/thawing cycles (book 44)

Konrad (1989) stated that repeated freezing and thawing cycles on clayey soils increase the effective void ratio and an increase of the permeability; volume, shear strength and compressibility change, together with the redistribution of pore water and particle and the appearance of cracks (Viklander, 1997); the effect is enhanced by the cyclic freeze/thaw event (Biggar and Neufeld, 1996). According with other studies (Benson and Othman (1993), Chamberlain and Ayorinde (1991)) this change occurs primarily between the first three freezing/thawing cycles.

2.10.3. Water availability

In a silty soil, the formation of ice lenses required a constant contribution of water, which is taken through capillarity from the unfrozen soil. A water shortage will produce thinner ice lenses and a negligible frost heave. The presence of coarse grained material into the soil reduces the availability of water; in fact water cannot rise for capillarity through this material. This concept is well explained in Figure 2.24.
Higher frozen water content in the soil means higher water content while thawing. As explained before, if the draining conditions are poor, the soil will be transformed into a mud without load capacity.
SCOPES OF THE THESIS
Chapter 3: Scopes of the thesis

This thesis has been commissioned by the FriGeo AB; actually the company has been hired to treat sludges in the Ragn-Sells AB treatment plant in Stockholm; the sludges are frozen in freezing pools, and thawed at open air; with this procedure the original sludge, that has a high liquid content, while thawing, becomes a solid and compact product with lower water content, easier to be transported and accepted in landfills. The company is interested in increasing the actual knowledge about the physics and the chemistry behind the freezing and thawing technique, in order to transpose it on the treatment of different sludges. Hence the decision to focus one part of the thesis in a general literature review.

The aim of the literature review was to resume the studies done so far regarding freezing and thawing of different kind of sludges and soils, to have a better knowledge about the physics and chemistry (ice front movement, flocs structure changing, water content variation...) behind this treatment, to know the sludge characteristics that can influence the success of the treatment and to understand which freezing parameters are most suitable for the studied sludge. The collected information has been used in the second part of the thesis.

An experimental part will be done as well, under interest of FriGeo AB: two “to-be-treated” sludges from the treatment plant will be characterized and treated in laboratory with different freezing conditions: the ultimate goal of the experiments is to find the most suitable treatment parameters (freezing temperature and number of cycles), thanks to which the final product of the particular sludge will have less water and oil content. Schematically:

Before entering in the treatment, the sludge is analysed; depending on its characteristics, the best parameters will be chosen to obtain the best final product. The experiments performed in this thesis will help in the choice of the best freezing parameters. Variables of the treatment are the parameters of the freezing apparatus; also some characteristics of the sludge can be modified to suit better to the treatment: for example, it is possible to reduce its moisture content, letting it rest for an appropriate amount of hours and then removing the supernatant.
MATERIALS AND METHODS
4.1. Pre-test 1

Before starting with the experiments on sludge samples, it has been decided to perform some pre-tests on soil samples in order to become familiar with the freezing apparatus and to decide which kind of experiments are feasible and really necessary to reach the aim of the thesis. This thesis has been commissioned by the company FriGeo AB, so it is compulsory to use boundary conditions that are similar to those that are used in the real field work. The first pre-test considers the influence of the water content on the freezing and thawing time of soil samples.

4.1.1. Samples

Two soil samples (S1 and S2) have been prepared starting from old soils used in the laboratory for other experiments. An industrial mixer has been used to homogenise the soils; water has been added to the samples in order to have different moisture contents: six sub-samples with different moisture contents have been prepared, as shown in Table 4.1. Also tap water has been tested to have a comparison.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Subsample#</th>
<th>Moisture content ratio[%]</th>
<th>Dry matter content ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1</td>
<td>37.2</td>
<td>62.8</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>41.9</td>
<td>58.1</td>
</tr>
<tr>
<td>S2</td>
<td>1</td>
<td>39.4</td>
<td>60.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>42.9</td>
<td>57.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>45.6</td>
<td>54.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>49.4</td>
<td>50.6</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.1: Soil sub-samples and moisture content ratio

The composition of the soil has not been taken into consideration in this pre-test.

4.1.2. Methods

The samples have been placed with spoon and spatula inside soil sample tubes of 10.2 cm of height, 5 cm of internal diameter and 2 mm thick; a temperature probe has been inserted in each sample in order to control with a computer their freezing and thawing status. After being closed with rubber stoppers, the tube samples have been placed in an industrial freezer. The freezer is provided with a timer that allows the temperature to be switched between two values. The freezing temperature has been set at -28°C and the thawing temperature at +12°C. The use of probes has allowed finding the necessary time to have a complete frozen and thawed sample; 4 complete freezing cycles have been performed. A final analysis of the dried samples has been discussed. In order to evaluate the freezing time, the model proposed by Lunardini (1981) has been used as example (Figure 4.1):
The pore water starts freezing when the temperature drops to $T_{SC}$; the supercooled water and the soil are in a metastable equilibrium that can be easily broken. The transformation of water into ice releases latent heat and the temperature reaches $T_f$. Free water starts freezing; for cohesionless soils with small specific surface areas, $T_f$ will be close to $0^\circ C$.; for fine-grained soils (silts and clays), the temperature depression ($\Delta T$) can be as much as $5^\circ C$. The release of latent heat slows down when there is shortage of free water and bond water starts freezing. At the temperature $T_e$ (at the end of the curvature) the free water and most of the bond water are frozen. The freezing time is given by the sum of the time necessary to freeze completely the free water and the bond water.
4.2. Pre-test 2
The influence of the dissolved ions on the freezing and thawing time has been studied using solutions of water with different concentration of NaCl.

4.2.1. Samples
Six solutions of salt and tap water have been prepared, varying the concentration of NaCl; the electro-conductivity has been measured for every solution, as shown in Table 4.2.

<table>
<thead>
<tr>
<th>Solutions #</th>
<th>Concentration NaCl [mol/l]</th>
<th>% NaCl by weight</th>
<th>Conductivity at 11°C [mS/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0000</td>
<td>0.0</td>
<td>0.176</td>
</tr>
<tr>
<td>2</td>
<td>0.0854</td>
<td>0.5</td>
<td>2.22</td>
</tr>
<tr>
<td>3</td>
<td>0.2501</td>
<td>1.4</td>
<td>5.14</td>
</tr>
<tr>
<td>4</td>
<td>0.7073</td>
<td>4.0</td>
<td>44.9</td>
</tr>
<tr>
<td>5</td>
<td>1.8896</td>
<td>9.9</td>
<td>119.3</td>
</tr>
<tr>
<td>6</td>
<td>4.2176</td>
<td>19.8</td>
<td>195.3</td>
</tr>
</tbody>
</table>

Table 4.2: Concentration and conductivity of NaCl solutions

The phase diagram of the binary system “water and NaCl” is shown in Figure 4.2. The concentrations of salt have been maintained below 23.3 wt%, marked by the horizontal line, in order to avoid a saturated solution. Salt water can be considered a different material from pure water.

![Figure 4.2: Phase diagram for Water/NaCl solution]

The concentrations and conductivities of the solutions have been plotted in graph, showed below in Figure 4.3.
4.2.2. Methods

The six solutions have been placed in plastic bottles of 100 mL. The temperature probes have been inserted in each bottle, trying to maintain them exactly in the centre; after this, the bottles have been closed with a stopper and placed in the freezer. The freezer is provided with a timer that allows the temperature to be switched between two values: the freezing temperature has been set at -28°C and the thawing temperature at +12°C. Three complete freezing/thawing cycles have been performed to collect enough information regarding freezing and thawing times of the solutions. The freezing point depression of each solution has been calculated as well, using the following standard formula:

$$\Delta T_f = K_f \cdot m \cdot i$$

Where:
- $\Delta T_f$ is the freezing point depression [°C];
- $K_f$ is the cryoscopic constant for the solvent [°C·kg/mol];
- $m$ is the molality of the solution [mol/kg];
- $i$ is the Van’t Hoff factor and represent the total number of ions resulted from the dissociation of the dissolved compound.

Thanks to the freezing point, it is possible to estimate the exact temperature in which the solution will start freezing, allowing a better recognition of the freezing and thawing time.

$$T_f' = T_f + \Delta T_f$$

Where:
- $T_f'$ is the new freezing temperature [°C];
- $T_f$ is the freezing temperature of the solvent [°C].

For what concern water as a solvent, it has a freezing temperature equal to 0°C and a cryoscopic constant $K_f$ equal to -1.86 °C·kg/mol. NaCl dissolves into $Na^+$ and $Cl^-$ ions; its Van’t Hoff factor is therefore 2.
4.3. Untreated sludge characterization

Sludges with different characteristics have been collected in order to have comparison between them and the performed freeze/thaw technique. The first step is, of course, a preliminary characterization of the untreated sludge. Knowing their origin, it is necessary to select proper and possible experiments, which would not damage the apparatus and that can provide reliable and comparable data. In the following chapters there will be described the experiments and relative procedures used to characterize the sludges. Due to the particular nature of the used sludges not all the experiments were found to be feasible.

4.3.1. Sludge 1

The first sludge has been taken from the recycling station of RagnSells in Stockholm; the sludge came principally from a workshop in Arlanda Airport, plus minor sludges collected all around the city of Stockholm. The sludge didn’t receive any preliminary treatment prior being sent to the laboratory for the experiments; for this reason the received sludge contains many extraneous objects (pieces of wood, cigarette filters, and pieces of metal...), gravels and sand. The sludge arrived in the laboratory into PE-HD containers; it had a liquid consistency; it was characterized by a prickly and acrid smell of petrol; for safety reasons, its analyses have been performed using an aerated mask. The colour of the sludge was completely black. Three phases have been observed: the solution phase is the biggest, followed by the solid phase (flocs, gravels...) and an oily phase. The following list shows all the analyses that have been performed on the sludge; some experiments have been abandoned due to impossibility of performance or because the results have shown their uselessness.

- pH, electroconductivity of the supernatant;
- density, moisture and dry ratio;
- volatile solids content;
- filterability and suspended solids concentration;
- sludge volume index;
- sludge compaction;
- grain size distribution.

4.3.2. Sludge 2

The second sludge has the same origin of the first one, but it has undergone into a preliminary process to remove part of its oil and water content; as a result the density was higher than the one of the previous sludge. It is still possible to recognize three phases: solid phase (composed again of flocs, extraneous objects, gravels and sand), solution phase and oily phase. The sludge arrived in the laboratory into metallic containers for paint. The following list shows all the analyses that have been performed on the sludge; not all the experiments performed previously have been performed on this kind of sludge, thanks to the experience gathered in the previous experiments.

- density, moisture and dry ratio;
- volatile solids content;
- grain size distribution.
4.3.3. Methods

In the following paragraphs the procedures and the warnings that have been used to characterize the sludges are discussed.

**pH, electroconductivity of the supernatant**

Before starting the analyses of pH and electroconductivity, the manuals of the pH-meter and conductivity-meter have been carefully read to see if the presence of oil can affect the lecture or, in the worst of the cases, ruin the probes. The pH can be analysed in the unaltered sludge, while the conductivity can be measured only in the clarified supernatant. To avoid any risk, pH and electroconductivity have been analysed only on the sludge supernatant deprived of the oily phase.

**Density, moisture and dry ratio**

Few mL of well mixed sludge have been placed into weighed crucibles. The weight of the sludge samples in each crucible has been registered \((M_S)\). The dry mass of each sample \((M_D)\) shall be determined at \((105 \pm 5)\) °C for 24 hours; the dry matter content ratio is calculated as follows:

\[
DR = 100 \cdot \frac{M_D}{M_W}
\]

(3.3.1)

where:

- **DR** is the dry matter content ratio [wt%];
- **M\_D** is the mass of the dried test portion [g];
- **M\_W** is the mass of undried test portion [g].

The moisture content ratio is calculated as follows:

\[
MC = 100 \cdot \frac{(M_W - M_D)}{M_W}
\]

(3.3.2)

where:

- **MC** is the moisture content ratio [wt%].

DR and MC are gravimetric percentages. The passage from the gravimetric moisture content ratio to the volumetric one is represented by the following formula:

\[
\Theta = MC \cdot \frac{\rho}{\rho_W}
\]

(3.3.3)

where:

- **\Theta** is the volumetric water content [%]
- **\rho** is the mass density of the sludge [g/L];
- **\rho\_W** is the density of the water [g/L].
Chapter 4: Materials and methods

The presence of oil can create several problems while drying the samples in the oven: the layer of oil that is formed over the sludge sample in the crucible does not allow an easy vaporization of the water that, on the contrary, sprays away oily droplets. To prevent this, a ceramic cover is necessary. The crucibles have to be weighed with their covers. The dry (bulk) density can be measured as well:

$$\rho_d = \rho \cdot DR/100$$  \hspace{1cm} (3.3.4)

where:

- $\rho_d$ is the dry density [g/L];

**Volatile solids content**

The volatile solids content ratio (representing the organic matter, OM) has been determined placing the dried samples in the oven at 550°C for 2 hours.

$$OM = 100 - \frac{MW - (MD - MS)}{MW} \cdot 100$$  \hspace{1cm} (3.3.5)

where:

- $MS$ is the mass of the residual solids (ashes) in the crucibles that are not burned [g];
- $OM$ is the organic matter content ratio of the sludge [wt%].

OM is a gravimetric percentage.

**Filterability and Suspended Solids (SS) concentration**

10 mL of fully mixed sludge have been filtered over a weighed GF/C filter paper using the micropore filter. When all the water has been removed, the filter has been carefully placed on a sheet of aluminium foil and then dried in the oven at 105°C. This took about 45-60 minutes. Once dry, the filter paper was removed and placed into the desiccator; after being reweighed, it has been possible to calculate the SS in g·L⁻¹.

$$SS = \frac{(B-A)/ C}{1000} \text{ g L}^{-1}$$  \hspace{1cm} (3.3.6)

Where:

- $A$ is the weight of the filter paper [g]
- $B$ the weight of the dried sludge and the filter paper [g]
- $C$ the volume of filtered sludge [mL].

The necessary time to have a complete filtration has been recorded.

**Sludge volume index**

The SVI is measured by filling a 1 litre graduated cylinder with well mixed sludge and allowing it to settle for 30 min. The volume of settled sludge ($V$) is then measured in mL.
Chapter 4: Materials and methods

SVI = \( \frac{V \cdot 1000}{SS} \) mL g\(^{-1}\)  \hspace{1cm} (3.3.7)

In this test the SS concentration is expressed in mg L\(^{-1}\). A good sludge should have an SVI <80 mL g\(^{-1}\) and a very good one around 50 mL g\(^{-1}\). An SVI >120 mL·g\(^{-1}\) indicates poor settling properties. The SVI test is severely affected by high SS concentrations with virtually no settlement occurring at concentrations >4000 mg·L\(^{-1}\). This experiment should show the differences in settleability between the original sludge and the treated sludges.

**Sludge compaction**

Sludge was placed in a 15 mL graduated centrifuge tube and centrifuged for 10 min at 9700g using a laboratory centrifuge. After centrifugation, the supernatant and the pellet volume were measured. The weight of the pellet was measured to find its concentration. The moisture content of the pellet was measured as well. The sludge compaction should simulate a mechanical treatment that removes water from the sludge; it has been supposed that only the free water is separated from the pellets. Since the freezing and thawing method transforms bond water into free water, this experiment should show how much free water has been created by the freezing treatment.

**Grain size distribution**

The study of the grain size distribution of this kind of sludges is particularly tricky due to the presence of oil and organic material that are only of hindrance. Oil and organic matter are not covered into the granulometry of the material; to bypass this problem the following cleaning procedure was implemented.

1. 400 g of untreated sludge sample have been placed into an aluminium container and dried at 105°C for 3 days to get rid of all the water, also the water that can be contained into the oily phase.
2. After being dried, the material has been mixed and placed in the oven at 200°C, to vaporize part of the oil. The material has to stay into the oven until it doesn’t shown any weight change. When ready, the material has to be gently grounded with a pestle in order to simplify the next steps.
3. 350 mL of solution of H\(_2\)O\(_2\) 10 %v/v were placed into a 2 liters Erlenmeyer flask; 60 g of material were incorporated gradually into the solution, maintaining it well mixed.
4. A 100°C water bath was prepared. The Erlenmeyer flask has been placed into the hot water bath, away from the heat source.
5. When bubbles start to appear into the flask, it has to be removed from the bath and carefully mixed with a slotted spoon; this operation is necessary to avoid a leakage of bubbles from the flask and a consequent loss of solid material that is transported with them. When the bubbles disappear, the flask can be replaced into the hot water bath, repeating this procedure until there are no more bubbles.
6. 150 mL of H\(_2\)O\(_2\) solution were added into the flask to remove the remaining organic matter; steps from n°5 were repeated.
7. The resulting material is divided into plastic bottles that will be placed in a centrifuge for 10 minutes, to divide pellets and supernatant. The supernatant has to be removed and replaced with distilled water, mixing it with the pellets for 20 seconds. Centrifuge again, remove the supernatant, add distilled water and centrifuge until the supernatant can be considered clean.

8. If the supernatant is not clean after several cleaning passages, it is necessary to repeat again from step number 3.

9. At this point the material is clean; after being dried it is ready to undergo the procedure for the standard grain size distribution.

The material is analysed through sieve analysis for the particles with a diameter greater than 0.063 mm and through sedigraph measurements for the particles with a diameter inferior than 0.063 mm.

- **Particle size distribution of coarse-grained material**
  As described in the standards ASTMD422-63 (2001), the distribution of particle sizes, or average grain diameter of coarse-grained soils (gravels and sands with a diameter greater than 0.063 mm), is obtained by screening a known weight of the soil through a stack of sieves of progressively finer mesh size. The particle diameter in the screening process is the maximum particle dimension to pass through the square hole of a particular mesh. A known weight of dry soil is placed on the largest sieve (the top sieve) and the nest of sieves is then placed on a sieve shaker, and shaken. The nest of sieves is dismantled, one sieve at a time. The soil retained on each sieve is weighed and the percentage of soil retained on each sieve is calculated. The results are plotted on a graph of percent of particles finer than a given sieve (particle size distribution curve) as the ordinate versus the logarithm of the particle sizes. Let $W_i$ be the weight of soil retained on the $i$th sieve from the top of the nest of sieves and $W$ be the total soil weight. The percent weight retained is:

$$\% \text{ Retained on \ ith \ sieve} = \frac{W_i}{W} \cdot 100 \quad (3.3.7)$$

The percent finer is:

$$\% \text{ Finer \ than \ ith \ sieve} = 100 - \sum_{i=1}^{n} (\% \text{ Retained on \ ith \ sieve}) \quad (3.3.8)$$

It is possible to use weight or mass indistinctly.

- **Particle size distribution of fine-grained material**
  The granulometry of the particles with diameter inferior than 0.063 mm has been studied through sedigraph measurements. Particle mass is measured directly via X-ray absorption. By measuring the rate at which particles fall under gravity through a liquid having known properties as described by Stokes’s law, the sedigraph determines the equivalent spherical diameter of particles ranging from 300 to 0.1 micrometers.
4.4. External conditions that influence the sludge consolidation: variation of temperature

As stated in many studies, cited in the literature review, the temperature at which the sludge is frozen is one of the key factors of its dewaterability and consolidation. The authors of these studies analysed the variation of freezing temperature principally on waste activated sludge and alum sludge; few studies have been performed on oily sludges and no studies on workshop sludges, like the one object of this thesis work.

4.4.1. Methods

Approximately 300 mL of well mixed sludge have been placed inside soil sample tubes of 17 cm of height, 5 cm of internal diameter and 2 mm thick. After being closed with rubber stoppers and insulator tape, a temperature probe has been inserted into one sample in order to control with a computer its freezing and thawing status; the tubes can now be placed in the freezer. The freezer is provided with a timer that allows the temperature to be switched between two values. Different values for the freezing temperature have been used: -5, -10, -20°C and the minimum temperature achievable by the freezer, -28°C; the thawing temperature on the other side was set at +20°C, room temperature. The tubes have been frozen for 24 hours. For each freezing temperature, two sludge tubes have been prepared, in order to perform several analyses, listed below. Some experiments have been abandoned due to impossibility of performance or because the results have shown their uselessness.

**pH, electroconductivity of the supernatant**
As described before, but on the treated sludge.

**Sludge compaction**
As described before, but on the treated sludge.

**Filterability and Suspended Solids (SS) concentration**
As described before, but on the treated sludge.

**Leaching test**
In order to evaluate the characteristics of the treated sludges at different freezing temperatures (and also freezing cycles as described later in this chapter), a “leaching” apparatus has been prepared, as shown in Figure 4.4. The apparatus is easily composed of a 1 mm sieve over which the frozen sludge sample is placed. The sieve is maintained over a beaker with a support (tripod). While thawing at room temperature, the sludge leachate is filtered inside a funnel by a filter paper and collected into the beaker. The filter should keep the eventual solid material that passes the sieve.
Chapter 4: Materials and methods

After 24 hours that the frozen sample has been placed over the sieve, the collected liquid is measured (volume, weight, density) and the remaining material over the sieve is analysed. DR, MC, OM and MS of the remaining material have been calculated using the procedures described before, with the aim of a comparison between the different freezing boundary conditions; the plastic limit PL has been measured as well. The plastic limit is used to characterize soils; it is the lowest moisture content, expressed as a percentage by weight, at which the soil can be rolled into threads 3 mm in diameter without breaking into pieces. This apparatus has been prepared thinking about the real conditions at which the treated sludge is subjected: it simulates what happens when the thawing sludge is placed over a permeable media, like compost or a grid; evaporation and leaching occur.

The following table (Table 4.3) resumes the experiments performed for every sample treated at different freezing temperatures. Not all the experiments have been performed for all the freezing conditions: the experience gathered while performing them demonstrates the ineffectiveness and uselessness of certain tests.
Chapter 4: Materials and methods

<table>
<thead>
<tr>
<th>Temperature</th>
<th>pH &amp; electroconductivity</th>
<th>Sludge compaction</th>
<th>Filterability &amp; SS concentration</th>
<th>Leaching test</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5°C</td>
<td>v</td>
<td>v</td>
<td>v</td>
<td>v</td>
</tr>
<tr>
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<td>x</td>
<td>x</td>
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</table>

<table>
<thead>
<tr>
<th>Temperature</th>
<th>pH &amp; electroconductivity</th>
<th>Sludge compaction</th>
<th>Filterability &amp; SS concentration</th>
<th>Leaching test</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5°C</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
<tr>
<td>-10°C</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
<tr>
<td>-20°C</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
<tr>
<td>-28°C</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
</tbody>
</table>

Table 4.3: performed experiments. X: not performed; V: performed.

4.5. External conditions that influence the sludge consolidation: variation of freezing/thawing cycles

The variation of freezing and thawing cycles is not a key factor in the consolidation of wastewater, alum or oily sludges; in fact it is hard to find citations regarding this subject in the literature. On the other hand, the number of freezing and thawing cycles influences the behaviour of a soil, as stated in the literature review. For this reason a series of experiments have been performed changing the number of freezing/thawing cycles for every used freezing temperature.

4.5.1. Methods

300 mL of well mixed sludge have been placed inside soil sample tubes of 17 cm of height, 5 cm of internal diameter and 2 mm thick. After being closed with rubber stoppers and insulator tape, a temperature probe has been inserted into a sample, in order to control with a computer the freezing and thawing status; at this point the tubes can be placed in the freezer. The freezer is provided with a timer that allows the temperature to be switched between two values: a freezing temperature and a thawing temperature. The freezing temperatures that have been used are the same as described previously: -5, -10, -20°C and -28°C; the thawing temperature was set at +20°C, near room temperature. The timer gives also the possibility to choose the number of freezing/thawing cycles: for every freezing temperature, three or five cycles have been performed. The tubes have been frozen for 24 hours and thawed for the same amount of hours. Like before, some experiments have been abandoned due to impossibility of performance or because the results have shown their uselessness.

**pH, electroconductivity of the supernatant**

As described before, but on the treated sludge.

**Sludge compaction**

As described before, but on the treated sludge.
**Filterability and Suspended Solids (SS) concentration**
As described before, but on the treated sludge.

**Leaching test**
As described before.

The following table (Table 4.4) resumes the experiments performed for every sample, treated at different freezing temperatures and cycles. Not all the experiments have been performed for all the freezing condition: the experience gathered while performing them demonstrates the ineffectiveness and uselessness of certain tests.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Number of cycles</th>
<th>pH &amp; electroconductivity</th>
<th>Sludge compaction</th>
<th>Leaching test</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5 °C</td>
<td>3</td>
<td>v</td>
<td>v</td>
<td>v</td>
</tr>
<tr>
<td>-10°C</td>
<td>3</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
<tr>
<td>-20°C</td>
<td>3</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
<tr>
<td>-28°C</td>
<td>3</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Number of cycles</th>
<th>pH &amp; electroconductivity</th>
<th>Sludge compaction</th>
<th>Leaching test</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5 °C</td>
<td>3</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
<tr>
<td>-10°C</td>
<td>3</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
<tr>
<td>-20°C</td>
<td>3</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
<tr>
<td>-28°C</td>
<td>3</td>
<td>x</td>
<td>x</td>
<td>v</td>
</tr>
</tbody>
</table>

Table 4.4: performed experiments. *x*: not performed; *v*: performed.
RESULTS AND DISCUSSION
5.1. Pre-test 1

These simple pre-tests have been used to become familiar with the apparatus, to find the necessary time for a sample to be totally thawed or frozen and to relate these times with the water content.

5.1.1. Freezing and thawing time

Data have been collected by the probes with an interval of 10 seconds and then analysed with the computer to find freezing and thawing times: the results are plotted into time vs. temperature curves. The sensors are not perfectly calibrated; in fact no one of the samples reaches the minimum temperature of the freezer. Figure 4.1 shows the trend of the temperature inside the samples in response to the freezer temperature; the freezer takes more or less one hour to pass from -28 to +12°C and 4 hours to reach completely the lowest temperature; the room temperature can be considered constant at +21°C.

The samples start freezing at -1°C, due to the presence of impurities (like salts) and to the composition of the soil (primarily fine-grained soil); this result agrees with what was explained in the literature review. In Figure 4.2 it is shown the conceptual model used to determine the necessary time for a sample to be totally frozen or thawed. The red curve represents the temperature of the freezer; the blue one represents the temperature of the sample. In A the freezer is near 0°C, becoming warmer and warmer: in this point the sample is supposed to start thawing. B is the point in which the temperature curve of the sample
becomes linear: the temperature increases linearly, that means that the sample is completely thawed. In C the freezer temperature goes below the 0°C line: the sample is supposed to start freezing. In D the temperature curve becomes linear: D represents the end of the transition between liquid state and solid state of the water in the sample (free water and most of the bond water are frozen). A-B represents the thawing time and C-D the respective time of freezing.

Following this model it has been possible to find for every sample the freezing and thawing time (Table 4.1).

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Subsample#</th>
<th>Freezing time [min]</th>
<th>Thawing time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1</td>
<td>160</td>
<td>181</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>208</td>
<td>210</td>
</tr>
<tr>
<td>S2</td>
<td>1</td>
<td>203</td>
<td>208</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>204</td>
<td>228</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>177</td>
<td>223</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>182</td>
<td>235</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>242</td>
<td>369</td>
</tr>
</tbody>
</table>

Table 4.1: Freezing and thawing time

5.1.2. Freezing time vs. Water content

For every sample, the freezing time has been correlated with the respective water content (Figure 4.3). An increase in water content increases the freezing time of the sample 1 (S1), while decreases it for what concern the sample 2 (S2). The tap water needs 4 hours to freeze completely. Probably some other parameters influence the freezing time of the soil samples. The number of samples was not enough to draw clear conclusions.
5.1.3. Thawing time vs. Water content

For every sample, the thawing time has been correlated with the respective water content (Figure 4.4). An increase in water content increases the thawing time of the sample 1 (S1); same results have been obtained with sample 2 (S2). The tap water needs more than 6 hours to thaw completely. The number of samples is not big enough to draw definite conclusions, but from these first results it seems that the thawing time is linearly dependent to the water content, of course in relation with the thawing temperature, sample geometry and volume.
5.2. Pre-test 2

The results that will be obtained with this test will clarify the relationship between freezing/thawing time and dissolved ions concentration. The total freezing time necessary to completely freeze a particular solution and the total thawing time necessary to thaw it will be used to compile a time calendar for the experiments on the sludges.

5.2.1. Freezing point depression and thawing/freezing time

Table 4.2 shows the temperatures at which solutions with different concentration of salt start freezing. Every freezing point corresponds to a line in the time vs. temperature graph (Figure 4.6), allowing a better recognition of the time necessary to have a complete frozen or thawed solution, as explained in Figure 4.5.

<table>
<thead>
<tr>
<th>Solutions #</th>
<th>Concentration NaCl [mol/l]</th>
<th>% NaCl by weight</th>
<th>Molality [mol/kg solvent]</th>
<th>Freezing point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0000</td>
<td>0.0</td>
<td>0.0000</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>0.0854</td>
<td>0.5</td>
<td>0.0854</td>
<td>-0.3</td>
</tr>
<tr>
<td>3</td>
<td>0.2501</td>
<td>1.4</td>
<td>0.2501</td>
<td>-0.9</td>
</tr>
<tr>
<td>4</td>
<td>0.7073</td>
<td>4.0</td>
<td>0.7073</td>
<td>-2.6</td>
</tr>
<tr>
<td>5</td>
<td>1.8896</td>
<td>9.9</td>
<td>1.8896</td>
<td>-7.0</td>
</tr>
<tr>
<td>6</td>
<td>4.2176</td>
<td>19.8</td>
<td>4.2176</td>
<td>-15.7</td>
</tr>
</tbody>
</table>

Table 4.2: Solutions and relative freezing points

The red line represents the temperature of the freezer, while the blue line is the temperature in the centre of the tube containing the solution. The line A-C represents the freezing point of the NaCl solution. Therefore the solution is considered to start thawing in A and start freezing in C. In B, the point in which the curve become straight, the solution is considered completely thawed. In D the solution is considered completely frozen. The distance between A and B represents the thawing time while the distance C-D is the time to have a completely frozen solution. Figure 4.6 shows the trend of the temperature inside the solutions in response to the freezer temperature; the freezer takes more or less one hour to pass from -28 to +12°C and 4 hours to reach the lowest temperature; the room temperature can be considered constant at +21°C. The horizontal lines represent the calculated freezing points and they match quite
well with the observed freezing and thawing trends of the first four solutions. Under -22°C the lectures of the temperature inside the tubes seem to be disturbed. This phenomenon may be due to two reasons: the first regards the phase change of the salt water at -21.1°C (mixed ice and salt crystals, as shown in Figure 3.1) that can disrupt the connection between the two metals with which the probes are made, and, as a result, the temperature in the tubes seems higher than the temperature inside the freezer. The latter considers the disruption a real phenomenon: the increase of temperature is due to the formation of ice from remained unfrozen saturated solution; when the ice is completely formed, the temperature starts decreasing again; following this hypothesis, there was not enough time for the sixth solution to reach the minimum temperature.

Following the conceptual model described before, it has been possible to find the freezing and thawing time of the different solutions (Table 4.3). Samples 5 and 6 have not a pattern that is similar to the other samples: it is hard to recognize the point in which the sample starts freezing and thawing and, for this reason, they have not been taken into consideration.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Freezing time [h:min]</th>
<th>Thawing time [h:min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>231</td>
<td>314</td>
</tr>
<tr>
<td>2</td>
<td>207</td>
<td>305</td>
</tr>
<tr>
<td>3</td>
<td>197</td>
<td>287</td>
</tr>
<tr>
<td>4</td>
<td>201</td>
<td>248</td>
</tr>
<tr>
<td>5</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>6</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 4.3: Freezing and thawing time of the solutions
5.2.2. Freezing time vs. Electroconductivity

For every sample, the freezing time has been correlated with the respective electroconductivity and NaCl molarity (Figure 4.7a, b). The freezing time decreases with the increase of salt concentration (and consequently increasing of electroconductivity).

5.2.3. Thawing time vs. Electroconductivity

For every sample, the thawing time has been correlated with the respective electroconductivity and NaCl molarity (Figure 4.8a, b). The freezing time decreases with the increase of salt concentration (and consequently increasing of electroconductivity).
5.3. Sludge 1 - Characterization

The first sludge was really hard to characterize: many experiments have been thought in order to characterize as well as possible the sludge, but due to its characteristics only few experiments had success. In this paragraph the results obtained on the untreated sludge are discussed; combined with the information showed in the literature review, these results should help to explain the behaviour of the sludge when it is frozen and thawed.

**pH, electroconductivity**

As already stated, the presence of oil can ruin the probes of a pH-meter and of a conductivity-meter; during the experiments it was noted how difficult it is to clean the apparatus after being in contact with the sludge. For this reason it has been decided to analyse the supernatant deprived of oil, extracting it with a syringe from the settled sludge. The supernatant pH was equal to 5.9 while the conductivity was 7.78 mS/cm.

**Density, moisture and dry ratio**

The mass density of the sludge is equal to 1152 g/L, slightly greater than that of water. To measure moisture and dry ratio, different subsamples have been prepared, in order to have a more uniform result and eliminate the errors due to the presence of extraneous objects in the sludge. The next table (Table 4.4) shows the moisture content ratio and the dry ratio obtained for the sludge:

<table>
<thead>
<tr>
<th>Sub-sample</th>
<th>M_W [g]</th>
<th>M_D [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.97</td>
<td>5.61</td>
<td>40.2</td>
<td>59.8</td>
</tr>
<tr>
<td>2</td>
<td>16.36</td>
<td>6.33</td>
<td>38.7</td>
<td>61.3</td>
</tr>
</tbody>
</table>

*Table 4.4: Moisture and dry ratio*

The average DR is 39.4 wt% while the average MC is 60.6 wt%. The measured dry density is equal to 454 g/L. The volumetric percentage of water in the sludge is 70%.

**Volatile solids content**

After ignition, the volatile solids of the sludge (equal to the organic content composed by oil and organic matter) have been calculated, as showed in Table 4.5:

<table>
<thead>
<tr>
<th>Sub-sample</th>
<th>M_W [g]</th>
<th>M_D [g]</th>
<th>M_S [g]</th>
<th>OM [wt%]</th>
<th>M_S [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.97</td>
<td>5.61</td>
<td>4.07</td>
<td>11.0</td>
<td>29.1</td>
</tr>
<tr>
<td>2</td>
<td>16.36</td>
<td>6.33</td>
<td>4.29</td>
<td>12.5</td>
<td>26.2</td>
</tr>
</tbody>
</table>

*Table 4.5: Volatile solids content*

The average organic matter (OM) in the sludge is equal to 11.7 wt% while the inorganic solid content, in average, is 27.7 wt%. The sum of organic matter (OM) and inorganic solids (M_S) represents the dry ratio (DR) of the sludge. A schematic representation of the sludge composition is shown in Figure 4.9.
The percentages of organic matter and inorganic solids in the dry ratio are 29.8 wt% and 70.2 wt% respectively. The sludge is composed by 70% in volume of water, from which its liquid consistency. The dry matter is composed by inorganic solids and oil plus organic matter, the organic material.

**Filterability and Suspended Solids (SS) concentration**

The filtration of the sludge takes really long time: to filter 10 mL of well mixed sludge is necessary more than one hour. In the paragraph 3.3.3 of the previous chapter it is described how to find the suspended solids of the sludge; Table 4.6 contains the results:

<table>
<thead>
<tr>
<th>#</th>
<th>Sludge volume [mL]</th>
<th>A - Filter paper [g]</th>
<th>B - Dried sludge + Filter paper [g]</th>
<th>SS [g/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.093</td>
<td>4.0</td>
<td>390.7</td>
</tr>
</tbody>
</table>

*Table 4.6: SS*

The SS concentration is lower than the bulk density of the sludge: dissolved material and oil are counted while analysing the bulk density, but escape from the filter while measuring the suspended solids concentration.

**Sludge volume index**

A one liter graduated cylinder has been filled with well mixed sludge. The chronometer has been started in order to begin the SVI test. Unfortunately the high suspended solids concentration made impossible a rapid subdivision in layers of the sludge. Also the colour of the sludge is not helpful in this kind of analyses. For this reason it has been decided to avoid these kinds of tests on the untreated sludge.

**Sludge compaction**

Three sludge samples have been placed into 15 mL graduated centrifuge tubes. After centrifuge, a measure of the different phases has been performed. A schematic representation of the sludge in the centrifuge tube before and after having been centrifuged is shown in Figure 4.10.
The results are shown in Table 4.7:

<table>
<thead>
<tr>
<th></th>
<th>Sludge [mL]</th>
<th>Oily phase [mL]</th>
<th>Water phase [mL]</th>
<th>Liquor [mL]</th>
<th>Pellet [mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>1</td>
<td>7.5</td>
<td>8.5</td>
<td>6.5</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>1</td>
<td>7.5</td>
<td>8.5</td>
<td>6.5</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>1.5</td>
<td>8</td>
<td>9.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 4.7: Volume of the sludge phases after compaction

Three phases are clearly visible after compaction of the sludge: oily phase (in average 7.8 %v/v), solid phase (the remaining pellets, in average 41.1 %v/v) and liquid phase (the supernatant, in average 51.1 %v/v). The oil is squeezed out from the pellets and floats over the water phase. The moisture content and dry matter ratio of the pellets have been measured, as shown in Table 4.8:

<table>
<thead>
<tr>
<th></th>
<th>Sludge [mL]</th>
<th>Sludge [g]</th>
<th>Pellet [g]</th>
<th>DM [wt%]</th>
<th>MC [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>16.74</td>
<td>8.61</td>
<td>61.1</td>
<td>38.9</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>17</td>
<td>9.25</td>
<td>60.0</td>
<td>40.0</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>17.54</td>
<td>8.36</td>
<td>59.6</td>
<td>40.4</td>
</tr>
</tbody>
</table>

Table 4.8: Gravimetric composition of the pellets after compaction

The average dry matter and moisture content are 60.2 wt% and 39.8 wt% respectively. The volumetric composition of the collected pellets has been calculated as well (Table 4.9):

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.065</td>
<td>8.61</td>
<td>38.9</td>
<td>3.4</td>
<td>0.034</td>
<td>51.6</td>
<td>48.4</td>
</tr>
<tr>
<td>2</td>
<td>0.065</td>
<td>9.25</td>
<td>40.0</td>
<td>3.7</td>
<td>0.037</td>
<td>56.9</td>
<td>43.1</td>
</tr>
<tr>
<td>3</td>
<td>0.055</td>
<td>8.36</td>
<td>40.4</td>
<td>3.4</td>
<td>0.034</td>
<td>61.5</td>
<td>38.5</td>
</tr>
</tbody>
</table>

Table 4.9: Volumetric composition of the pellets after compaction

The average water content in the pellets is 56.7 %v/v and the average dry matter is 43.3 %v/v. Finally, the compacted sludge can be resumed as follow (Figure 4.11a):
Chapter 5: Results and discussion

The green slice represents the pellet collected in the tubes.

**Grain size distribution**

The material has been cleaned as described in Chapter 4, paragraph 4.3.3. The resulting dry material is a grey mixture of particles. 18.58 grams of material have been analysed.

- **Particle size distribution of coarse-grained material**
  A total mass of 6.31 g of material has been retained over all the sieves, that means that there are 12.27 g of material finer than 0.063 mm, equivalent to the 66% of the total. Table 4.10 contains all the data collected after the sieving of the coarse-grained material:

<table>
<thead>
<tr>
<th>Sieve diameter [mm]</th>
<th>Retained on i\textsuperscript{th} sieve [g]</th>
<th>% Retained on i\textsuperscript{th} sieve</th>
<th>% Cumulative mass greater than i\textsuperscript{th} sieve</th>
<th>% Cumulative mass finer than i\textsuperscript{th} sieve</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.01</td>
<td>0.2</td>
<td>0.2</td>
<td>99.8</td>
</tr>
<tr>
<td>1</td>
<td>0.06</td>
<td>1.0</td>
<td>1.1</td>
<td>98.9</td>
</tr>
<tr>
<td>0.5</td>
<td>1.3</td>
<td>20.6</td>
<td>21.7</td>
<td>78.3</td>
</tr>
<tr>
<td>0.25</td>
<td>1.34</td>
<td>21.2</td>
<td>42.9</td>
<td>57.1</td>
</tr>
<tr>
<td>0.125</td>
<td>2.36</td>
<td>37.4</td>
<td>80.3</td>
<td>19.7</td>
</tr>
<tr>
<td>0.063</td>
<td>1.24</td>
<td>19.7</td>
<td>100.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Table 4.10: Sieving analyses*

From these data it is possible to draw the granulometry histogram (Figure 4.12) and the grain-size distribution curve (Figure 4.12) for the studied material.
• **Particle size distribution of fine-grained material**

The 66% of the initial material passed through the 0.063 mm sieve. Thanks to sedigraph measurements it has been possible to find directly the granulometry of this material. Figure 4.14 shows the granulometry histogram (mass frequency) while Figure 4.15 represents the grain-size distribution curve.
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Figure 4.14: Granulometry histogram

Figure 4.15: Grain-size distribution curve, cumulative finer mass percent vs. diameter

The complete analysis performed on the material with the particles diameter inferior than 0.063 mm is described in APPENDIX A.
5.4. Sludge 1 - External conditions that influence the sludge consolidation: variation of temperature

5.4.1. Freezing temperature -5°C, thawing temperature +20°C, 1 cycle

Freezing and thawing time
Different sludge tubes have been frozen, in order to have samples to be analysed after 1 cycle and after 3 cycles. The temperature probes inserted in the tubes allowed the lecture of the freezing and thawing time, as shown in Figure 4.16. The sludge in the 17 cm height tubes needs 12 hours to be totally frozen and other 10 hours to reach the temperature of -5°C. The freezing point of the sludge is near -1°C, which means that the sludge is mainly composed of fine-grained particles and contains dissolved solids plus polluting agents that can influence its freezing point. The sample is completely thawed after 2 hours, but the interior part needs other 5 hours to reach the room temperature. The room temperature can be considered constant at +23°C. The freezer is not capable to maintain a constant temperature of -5°C, but it continues to oscillate between -4°C and -6°C with an average of -5°C.

Frozen sample and leaching test
After one freezing cycle, just before the beginning of the thawing phase, a tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. While extracting the solidified sludge, some liquor flowed away: oil and a little unfrozen leachate. After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.11.
Chapter 5: Results and discussion

<table>
<thead>
<tr>
<th>#</th>
<th>( M_0 ) [g]</th>
<th>( M_D ) [g]</th>
<th>( M_S ) [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
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<td>63.3</td>
<td>36.7</td>
<td>18.7</td>
<td>44.6</td>
</tr>
</tbody>
</table>

Table 4.11: DR, OM, MC, MS of the treated sludge

In average, DR = 63.2 wt\% and MC = 36.8 wt\%; OM = 18.7 wt\% and Ms = 44.6 wt\%, with a mass ratio OM:Ms equal to 1:2.39. 95 mL of leachate have been collected in the beaker; 2 subsamples of 10 mL each have been analysed; the results are shown in Table 4.12.

<table>
<thead>
<tr>
<th>#</th>
<th>( M_0 ) [g]</th>
<th>( M_D ) [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
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<td>1.1</td>
<td>98.9</td>
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<tr>
<td>2</td>
<td>8.7</td>
<td>0.13</td>
<td>1.5</td>
<td>98.5</td>
</tr>
</tbody>
</table>

Table 4.12: Characteristics of the leachate

The density of the leachate is equal to 871.5 g/L, lower than the one of the water, due to the presence of oil that has not been trapped by the filter; the dry density \( \rho_d \) is 11.5 g/L that means 1.1 g of dry material in 95 mL of leachate. The filter has collected 0.78 g of dry material (oil and suspended solids). Less than 2 grams of dry material were lost from the sieve. The plastic limit PL of the collected solid material over the sieve was 27.4 %.

**Treated sludge properties**

The treated sludge supernatant has conductivity equal to 6.76 mS/cm. When thawed in the tube, an upper oily layer is visible, although really thin; in the moment of empty the tube from the thawed sludge, the first part that flowed away was liquor and floating materials, while the latter was a semi-compacted material. The tube resulted to be easier to clean than a tube containing untreated sludge.

**Filterability and Suspended Solids (SS) concentration**

One hour has been necessary to filtrate 10 mL of treated and mixed sludge; Table 4.13 contains the data obtained from the filtration and the resulted concentration of suspended solids

<table>
<thead>
<tr>
<th>#</th>
<th>Sludge volume [mL]</th>
<th>A - Filter paper [g]</th>
<th>B - Dried sludge + Filter paper [g]</th>
<th>SS [g/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.093</td>
<td>4.26</td>
<td>416.7</td>
</tr>
</tbody>
</table>

Table 4.13: SS

The result is really similar to the one obtained with the untreated sludge; there is a little increment of suspended solids in the solution due probably to a bacterial cell disruption and consequent release of particles, but the effect is negligible. Since this experiment requires a long time to be performed and it is really hard to clean the used apparatus, it has been decided to abandon this experiment.
**Sludge compaction**

As stated in the literature review, the freezing treatment is supposed to modify the structure of the flocs and free part of their bond water. The compaction test should prove this statement: the pellet of the treated and compacted sludge should contain lower moisture content than the pellet of the untreated and compacted sludge, since the treated sludge should have more free water, which is easily removed with the compaction. To confirm this hypothesis, a tube of treated and thawed sludge has been gently mixed and three sub-samples have been taken and compacted. After being centrifuged, the following data have been collected:

<table>
<thead>
<tr>
<th></th>
<th>Sludge [mL]</th>
<th>Oily phase [mL]</th>
<th>Water phase [mL]</th>
<th>Liquor [mL]</th>
<th>Pellet [mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>1.5</td>
<td>10.5</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>1.5</td>
<td>10</td>
<td>11.5</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>1.5</td>
<td>10</td>
<td>11.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

*Table 4.14: Volume of the sludge phases after compaction*

Three phases are clearly visible after compaction of the sludge: oily phase (in average 10 \%v/v), solid phase (the remaining pellets, in average 22.2 \%v/v) and water phase (the supernatant, in average 67.8 \%v/v). The moisture content $MC'$ of the pellet was 43.5 wt\% and the dry matter ratio 56.5 wt\%. The liquid phase is much higher than the one of the original sludge because the treated sludge has not been really well mixed; in any case the final comparison is done on the moisture content of the pellets.
5.4.2. Freezing temperature -10°C, thawing temperature +20°C, 1 cycle

**Freezing and thawing time**

Different sludge tubes have been frozen, in order to have enough material to analyse. The temperature probes inserted in the tubes allowed the lecture of the freezing and thawing time, as shown in Figure 4.17. The sludge in the 17cm height tubes needs 4 hours and a half to be totally frozen and other 3 hours to reach the temperature of -10°C. The freezing point of the sludge is near -1°C, which means that the sludge is mainly composed of fine-grained particles and contains dissolved solids plus polluting agents that influence its freezing point. The sample is completely thawed after 4 hours, but the interior part needs other 6 hours to reach the room temperature. The room temperature can be considered constant at +23°C. The freezer is not capable to maintain a constant temperature of -10°C, but it continues to oscillate between -8.7°C and -11.2°C with an average of -10°C.

![Figure 4.17: Freezing and thawing time](image)

**Frozen sample and leaching test**

After one freezing cycle at -10°C, just before the beginning of the thawing phase, a tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. While extracting the solidified sludge, little liquor flowed away: the freezing temperature is low enough to freeze also the oil. Figure 4.18 shows the frozen sample: the rapid freezing time didn’t let the suspended material to settle; in fact the frozen sludge has a uniform black colour. The top is lighter, probably a thin layer of frozen oil. Furthermore, the top layer shows concentric lines: the ice front that advances inside the sample.
After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.15.

<table>
<thead>
<tr>
<th></th>
<th>$M_W$ [g]</th>
<th>$M_0$ [g]</th>
<th>$M_S$ [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.1</td>
<td>9.26</td>
<td>6.64</td>
<td>62.8</td>
<td>37.2</td>
<td>17.8</td>
<td>45.0</td>
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<tr>
<td>2</td>
<td>24.15</td>
<td>8.35</td>
<td>5.86</td>
<td>64.8</td>
<td>35.2</td>
<td>19.3</td>
<td>45.5</td>
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<tr>
<td>3</td>
<td>20.13</td>
<td>6.3</td>
<td>4.39</td>
<td>64.4</td>
<td>35.6</td>
<td>19.5</td>
<td>44.9</td>
</tr>
</tbody>
</table>

Table 4.15: DR, OM, MC, MS of the treated sludge

In average, DR = 64.0 wt% and MC = 36.0 wt%; OM = 18.9 wt% and Ms = 45.1 wt%, with a mass ratio OM:Ms equal to 1:2.39. 97 mL of leachate have been collected in the beaker; 1 subsample of 10 mL has been analysed; the results are shown in Table 4.16.

<table>
<thead>
<tr>
<th></th>
<th>$M_W$ [g]</th>
<th>$M_0$ [g]</th>
<th>$M_S$ [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>9.14</td>
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<td>0.05</td>
<td>1.3</td>
<td>98.7</td>
<td>0.8</td>
<td>0.5</td>
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</table>

Table 4.16: Characteristics of the leachate

The density of the leachate is equal to 981.3 g/L, slightly lower than the one of the water, due to the presence of oil; the dry density $\rho_d$ is 12 g/L that means 1.2 g of dry material in 97 mL of leachate. The filter has collected 0.35 g of dry material (oil and suspended solids). Less than 2 grams of dry material were lost from the sieve. The plastic limit PL of the collected solid material over the sieve was 25.3 %.

**Treated sludge properties**

The treated sludge supernatant has conductivity equal to 6.56 mS/cm. When thawed in the tube, an upper oily layer is visible, although really thin; in the moment of empty the tube from the thawed sludge, the first part that flowed away was liquor and floating materials, while the latter was a semi-compacted material.
5.4.3. Freezing temperature -20°C, thawing temperature +20°C, 1 cycle

**Freezing and thawing time**

Different sludge tubes have been frozen, in order to have enough material to analyse. The temperature probes inserted in the tubes allowed the lecture of the freezing and thawing time, as shown in Figure 4.19. The sludge in the 17 cm height tubes needs 2 hours and a half to be totally frozen and other 2 hours to reach the temperature of -20°C. The freezing point of the sludge is near -1°C: the sludge is mainly composed of fine-grained particles and contains dissolved solids plus polluting agents that influence its freezing point. The sample is completely thawed after 3 hours and a half, but the interior part needs other 4 hours to reach the room temperature. The room temperature can be considered constant at +23°C. The freezer is not capable to maintain a constant temperature of -20°C, but it continues to oscillate between -22°C and -20°C with an average of -21°C. The temperature probes read the temperature with an error of ±1°C; for this reason the temperature of the frozen sample appears to be inferior of the one of the freezer.

![Figure 4.19: Freezing and thawing time](image)

**Frozen sample and leaching test**

After one freezing cycle at -20°C, just before the beginning of the thawing phase, a tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. The sludge was so hard that it has been impossible to extract the probe which has been cut. Extracting the solidified sludge was harder than extracting the sludge treated at lower temperatures; no liquor flowed away. Figure 4.20 shows the frozen sample: despite the rapid freezing time, a subdivision of layers is visible: a thin first layer composed principally of frozen oil and floating substances, a second larger and lighter layer and the final layer composed of dark frozen sludge. Furthermore, the top layer shows concentric lines of ice front.
After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.17.

<table>
<thead>
<tr>
<th>#</th>
<th>MW [g]</th>
<th>MD [g]</th>
<th>MS [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
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<td>6.28</td>
<td>64.5</td>
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<td>19.9</td>
<td>44.6</td>
</tr>
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<td>12.62</td>
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<td>64.1</td>
<td>35.9</td>
<td>21.7</td>
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</tr>
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<td>16.35</td>
<td>10.75</td>
<td>7.53</td>
<td>65.7</td>
<td>34.3</td>
<td>19.7</td>
<td>46.1</td>
</tr>
</tbody>
</table>

Table 4.17: DR, OM, MC, Ms of the treated sludge

In average, DR = 64.8 wt% and MC = 35.2 wt%; OM = 20.4 wt% and Ms = 44.3 wt%, with a mass ratio OM:Ms equal to 1:2.17. 101 mL of leachate have been collected in the beaker; 2 subsamples of 10 mL each have been analysed; the results are shown in Table 4.18.

<table>
<thead>
<tr>
<th>#</th>
<th>MW [g]</th>
<th>MD [g]</th>
<th>MS [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.09</td>
<td>0.13</td>
<td>0.06</td>
<td>1.4</td>
<td>98.6</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>8.93</td>
<td>0.13</td>
<td>0.07</td>
<td>1.5</td>
<td>98.5</td>
<td>0.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 4.18: Characteristics of the leachate

The density of the leachate is equal to 991.8 g/L, really similar to the one of the water; the dry density $\rho_d$ is 13 g/L that means 1.3 g of dry material in 101 mL of leachate. The filter has collected 0.32 g of dry material (oil and suspended solids). Less than 2 grams of dry material were lost from the sieve. The plastic limit PL of the collected solid material over the sieve was 27.3 %.

**Treated sludge properties**

The treated sludge supernatant has conductivity equal to 7.72 mS/cm.
5.4.4. Freezing temperature -28°C, thawing temperature +20°C, 1 cycle

**Freezing and thawing time**

Different sludge tubes have been frozen, in order to have enough material to analyse. The temperature probes inserted in the tubes allowed the lecture of the freezing and thawing time, as shown in Figure 4.21. The sludge in the 17 cm height tubes needs 2 hours and to be totally frozen and other 2 hours to reach the temperature of -28°C. The freezing point of the sludge is near -1°C: the sludge is mainly composed of fine-grained particles and contains dissolved solids plus polluting agents that influence its freezing point. The sample is completely thawed after 3 hours and a half, but the interior part needs other 4 hours to reach the room temperature. The room temperature can be considered constant at +23°C. The freezer can maintain a constant temperature of -28°C. The temperature probes read the temperature with an error of ±1°C; for this reason the temperature of the frozen sample appears to be inferior of the one of the freezer, which cannot be true.

![Figure 4.21: Freezing and thawing time](image)

**Frozen sample and leaching test**

After one freezing cycle at the minimum freezer temperature, just before the beginning of the thawing phase, a tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. Extracting the solidified sludge was harder than extracting the sludge treated at lower temperatures; no liquor flowed away. Figure 4.22 shows the frozen sample: no layers are visible in the frozen sample; the top seems covered with a frozen stratum of oil.
After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.19.

<table>
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<tr>
<th>#</th>
<th>M_w [g]</th>
<th>M_o [g]</th>
<th>M_s [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>MS [wt%]</th>
</tr>
</thead>
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<td>16.0</td>
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<td>16.99</td>
<td>10.93</td>
<td>7.8</td>
<td>64.3</td>
<td>35.7</td>
<td>18.4</td>
<td>45.9</td>
</tr>
<tr>
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<td>16.33</td>
<td>10.01</td>
<td>7.21</td>
<td>61.3</td>
<td>38.7</td>
<td>17.1</td>
<td>44.2</td>
</tr>
</tbody>
</table>

Table 4.19: DR, OM, MC, MS of the treated sludge

In average, DR = 62.4 wt% and MC = 37.6 wt%; OM = 17.2 wt% and M_s = 45.3 wt%, with a mass ratio OM:M_s equal to 1:2.63. 99 mL of leachate have been collected in the beaker; one subsample of 10 mL has been analysed; the results are shown in Table 4.20.

<table>
<thead>
<tr>
<th>#</th>
<th>M_w [g]</th>
<th>M_o [g]</th>
<th>M_s [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>MS [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.29</td>
<td>0.11</td>
<td>0.05</td>
<td>1.2</td>
<td>98.8</td>
<td>0.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 4.20: Characteristics of the leachate

The density of the leachate is equal to 987.5 g/L, really similar to the one of the water; the dry density ρ_d is 11 g/L that means 1.1 g of dry material in 99 mL of leachate. The filter has collected 0.34 g of dry material (oil and suspended solids). Less than 2 grams of dry material were lost from the sieve. The plastic limit PL of the collected solid material over the sieve was 26.2 %.

Treated sludge properties

The treated sludge supernatant has conductivity equal to 7.73 mS/cm.
5.4.5. Comparison

According to the requests of FriGeo AB, the ultimate goal of the experiments is to find the proper treatment (freezing temperature and number of cycles), thanks to which the final product will have less water and oil content. To find this treatment it is necessary to perform different comparison between the obtained results. This section will compare the experiments performed at different freezing temperatures with one freezing cycle.

**Freezing and thawing time**

The first immediate comparison that can be performed is between the different freezing and thawing times. Of course, a sample treated with a lower temperature will take less time to freeze and more time to thaw, while a sample treated at higher temperature will act in the opposite way. The sludge tubes don’t represent perfectly what happens in reality, but give an idea of how much time a sample needs to freeze and thaw; time is money: long freezing time or long thawing time give no benefits to a treatment plant. Moreover, maintain a low freezing temperature for a long time can be expensive too. It is necessary to find a compromise between freezing temperature, freezing costs and results. Table 4.21 shows the freezing and thawing times versus freezing temperatures.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Freezing time [min]</th>
<th>Thawing time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5</td>
<td>645</td>
<td>69</td>
</tr>
<tr>
<td>-10</td>
<td>276</td>
<td>160</td>
</tr>
<tr>
<td>-20</td>
<td>149</td>
<td>202</td>
</tr>
<tr>
<td>-28</td>
<td>122</td>
<td>222</td>
</tr>
</tbody>
</table>

*Table 4.21: Freezing and thawing time*

The results can be compared in graphs, to have a better overview of the freezing phenomena (see Figure 4.23a and 4.23b).

The total treatment time (freezing time plus thawing time) required is shown in Figure 4.24:
At -5°C the treatment time is too high and so the relative costs. Under -20°C it is more expensive to maintain the treatment temperature. For this reasons, the treatments should be performed in a range between -10°C and -20°C. This analysis doesn’t take into account the final product of the freezing treatment.

**Conductivity**

The following table (Table 4.22) compares the conductivities measured from the sludges treated with different freezing temperatures:

<table>
<thead>
<tr>
<th>Treatment temperatures [°C]</th>
<th>Untreated</th>
<th>-28</th>
<th>-20</th>
<th>-10</th>
<th>-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity [mS/cm]</td>
<td>7.78</td>
<td>7.73</td>
<td>7.72</td>
<td>6.56</td>
<td>6.76</td>
</tr>
</tbody>
</table>

*Table 4.22: conductivities for different treatment temperatures*

As cited in the literature review, the freezing treatment is supposed to break the bacterial cells membranes, freeing suspended particles and ions into the sludge solution. This effect is influenced by the freezing temperature and by its rate; with a slow rate (low temperature) the growth of well formed ice crystals disrupts the cell membrane, increasing the conductivity of the suspension; in a fast freezing rate condition, the formation of ice dendrites doesn’t alter the structure of the cells and consequently even the conductivity. This doesn’t seem to be the case of the sludge object of these experiments: the conductivity is only slightly altered by the changing of freezing temperatures.

**Compaction test**

The compaction test should be a good expedient to analyse the structural modification of the sludge after treatment. The moisture contents of the pellets obtained from the treated sludges are compared with the untreated one because they should give an idea of how much bond water has been released with the freezing treatment: less moisture content in the treated pellet
means that the water can flow away more easily. Unfortunately the used sludge appears not to be influenced by the freezing treatment; the compaction test has been performed only on the untreated sludge (to have also more information about its composition) and on the sludge treated with one freezing cycle at -5°C. The results are shown in Table 4.23:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture content of the pellet [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated sludge</td>
<td>39.8</td>
</tr>
<tr>
<td>Freezing temperature -5°C, thawing temperature +20°C, 1 cycle</td>
<td>43.5</td>
</tr>
</tbody>
</table>

Table 4.23: Pellets moisture content

The moisture content of the pellet collected from the compaction of the treated sludge should be inferior to the one of the untreated sludge. This discrepancy could be caused by the mixing of the treated sludge prior of its placement in the centrifuge tubes; this mixing can cause the rupture of the newly formed structures in the sludge (due to freezing and thawing) and thus nullify the compaction test. For this reason no other compaction tests for the “1 cycle” tests have been performed.

**Leaching test**

In this test the structure of the thawed sludge is not altered by external factors, and thus it can be considered reliable and corresponding of what happens in reality. The characteristics of the treated sludges obtained through the leaching test are compared in this paragraph; moisture content, dry matter ratio, organic matter and inorganic matter are shown and compared with the characteristics of the untreated sludge.

- **Moisture content:**

  The moisture content of the untreated sludge is compared with those of the treated sludges. The following table (Table 4.24) resumes the results shown before:

<table>
<thead>
<tr>
<th>Untreated sludge</th>
<th>Freezing temperature [°C]</th>
<th>-5</th>
<th>-10</th>
<th>-20</th>
<th>-28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content [wt%]</td>
<td>60.6</td>
<td>36.8</td>
<td>36</td>
<td>35.2</td>
<td>37.2</td>
</tr>
</tbody>
</table>

Table 4.24: Moisture content of the untreated sludge and the leached sludges

Figure 4.25 plots the data shown above; the red line represents the moisture content of the untreated sludge, while the blue line represents the variation of moisture content in the leached sludge treated at different freezing temperatures.
The final product of the leaching test after 24 hours is a soil-like material with lower moisture content than the untreated sludge: the original sludge loses more or less 60% of its water content after freezing and thawing over a permeable stratum, no matter which freezing temperatures have been used. The lowest water content is reached with the treatment at -20 °C, while the highest at -28 °C; the difference is not so high, but it can be due to a change in the ice structure, from columnar to dendritical. At -28°C the faster freezing rate doesn’t allow a good compaction of the solid material with a loss in bound water, and therefore the highest water content after thawing and leaching.

- **Composition of the dry content ratio**

The dry matter is composed of organic material, inorganic solids and oil. After the leaching, part of the oil flows away and also part of the dissolved solids; the amount of these losses depends on the freezing treatment with which the sludge has been subjected. The collected dry material over the sieve varies from freezing condition to freezing condition; in the following table (Table 4.25) the dry content ratios (DR) are resumed:

<table>
<thead>
<tr>
<th>Treating temperature [°C]</th>
<th>Collected material over the sieve [g]</th>
<th>DR [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5</td>
<td>213.1</td>
<td>63.2</td>
<td>18.7</td>
<td>44.6</td>
</tr>
<tr>
<td>-10</td>
<td>213.3</td>
<td>64</td>
<td>18.9</td>
<td>45.1</td>
</tr>
<tr>
<td>-20</td>
<td>216.5</td>
<td>64.8</td>
<td>20.4</td>
<td>44.3</td>
</tr>
<tr>
<td>-28</td>
<td>209.6</td>
<td>62.4</td>
<td>17.2</td>
<td>45.3</td>
</tr>
</tbody>
</table>

*Table 4.25: Composition of the dry matter*

The following graph (Figure 4.26) plots the data discussed above:
Chapter 5: Results and discussion

Figure 4.26: Gravimetric content of the final product after leaching

To compare this data with the untreated sludge, it is necessary to convert the gravimetric content ratios (wt%) in masses.

\[ M = \frac{\text{wt\%} \cdot M_t}{100} \]

The total mass of the collected samples over the sieve (M_t) is shown in Table 4.25; the average mass of the untreated sample (M_U) of sludge in the tube is given by the product between the sludge density (\( \rho \)) and the tube volume (V_T):

\[ M_U = \rho \cdot V_T = 1152 \frac{g}{L} \cdot 0.300L = 345.6g \]

Figure 4.27 shows the composition of the untreated and treated sludges:

Figure 4.27: Comparison between the untreated and the treated sludges
Chapter 5: Results and discussion

The discussion regarding the water content has been done in the previous paragraph. It is not wrong to consider that all the inorganic material $M_S$ is trapped over the sieve and that the liquor is the only thing that passes it. From the previous data and graphs it is possible to conclude that very little organic matter flows through the sieve: the oil seems to stay trapped inside the zots and the inorganic solids. Only at -28°C it seems that there is a little loss of oil from the frozen sludge, but it is insignificant.

• **Plastic limit**

The plastic limit comparison should show if different freezing temperatures produce an eventual modification of the solid structure of the treated sludge. The next table (Table 4.26) resumes the plastic limits $PL$ found in each test:

<table>
<thead>
<tr>
<th>Test</th>
<th>Plastic limit [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freezing temperature -5°C, thawing temperature +20°C, 1 cycle</td>
<td>27.4</td>
</tr>
<tr>
<td>Freezing temperature -10°C, thawing temperature +20°C, 1 cycle</td>
<td>25.3</td>
</tr>
<tr>
<td>Freezing temperature -20°C, thawing temperature +20°C, 1 cycle</td>
<td>27.3</td>
</tr>
<tr>
<td>Freezing temperature -28°C, thawing temperature +20°C, 1 cycle</td>
<td>26.2</td>
</tr>
</tbody>
</table>

*Table 4.26: Plastic limits of the treated and leached sludges*

The results show that a clear modification of the sludge structure has not occurred when changing the freezing temperature of the treatment. The following graph (Figure 4.28) better clarifies what has been stated before:

The plastic limit can be considered constant, with an average of 26.6 wt%.
5.5. Sludge 1 - External conditions that influence the sludge consolidation: number of freezing/thawing cycles

5.5.1. Freezing temperature -5°C, thawing temperature +20°C, 3 cycle

Freezing and thawing time
As in paragraph 5.4.1.

Frozen sample and leaching test
After three freezing cycles at -5°C, just before the beginning of the thawing phase, a tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. While extracting the solidified sludge, some liquor flowed away; some oil is not completely trapped. Figure 4.29 shows the frozen sample: the freezing cycles allowed the sedimentation of the suspended solids, thus the division in layers. The top layer contains air and gas bubbles, the second layer is clarified water, while the third layer is compacted frozen sludge.

![Figure 4.29: Frozen sludge sample; a) top; b) side](image)

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.27.

<table>
<thead>
<tr>
<th>#</th>
<th>M_w [g]</th>
<th>M_d [g]</th>
<th>M_s [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>M_s [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>6.47</td>
<td>4.57</td>
<td>64.7</td>
<td>35.3</td>
<td>19.0</td>
<td>45.7</td>
</tr>
<tr>
<td>2</td>
<td>15.68</td>
<td>10.09</td>
<td>7</td>
<td>64.3</td>
<td>35.7</td>
<td>19.7</td>
<td>44.6</td>
</tr>
<tr>
<td>3</td>
<td>11.69</td>
<td>7.55</td>
<td>5.3</td>
<td>64.6</td>
<td>35.4</td>
<td>19.2</td>
<td>45.3</td>
</tr>
</tbody>
</table>

Table 4.27: DR, OM, MC, MS of the treated sludge

In average, DR = 64.5 wt% and MC = 35.5 wt%; OM = 19.3 wt% and M_s = 45.2 wt%, with a mass ratio OM:M_s equal to 1:2.34. 93 mL of leachate have been collected in the beaker; 2 subsamples of 10 mL each have been analysed; the results are shown in Table 4.28.
Chapter 5: Results and discussion

<table>
<thead>
<tr>
<th>#</th>
<th>$M_W$ [g]</th>
<th>$M_0$ [g]</th>
<th>$M_S$ [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.12</td>
<td>0.12</td>
<td>0.06</td>
<td>1.3</td>
<td>98.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>9.14</td>
<td>0.15</td>
<td>0.09</td>
<td>1.6</td>
<td>98.4</td>
<td>0.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 4.28: Characteristics of the leachate

The density of the leachate is equal to 984.8 g/L, slightly lower than the one of the water, due to the presence of oil that has not been trapped by the filter; the dry density $\rho_d$ is 13.5 g/L that means 1.3 g of dry material in 93 mL of leachate. The filter has collected 0.4 g of dry material (oil and suspended solids). Less than 2 grams of dry material were lost from the sieve. The plastic limit PL of the collected solid material over the sieve was 25.2 %.

**Treated sludge properties**

One frozen sludge sample has been let thawing at room temperature inside the soil tube for 24 hours; as a result part of the suspended particles settled. Paying attention not to extract some floating oil, part of the supernatant solution has been collected with a syringe: the corresponding conductivity was 7.65 mS/cm. Since the result is similar to those obtained previously, it has been decided not to analyse the conductivity in the subsequent experiments.

**Sludge compaction**

A tube of treated and thawed sludge has been gently mixed and three sub-samples have been taken and compacted. After being centrifuged, the following data have been collected:

<table>
<thead>
<tr>
<th>#</th>
<th>Sludge [mL]</th>
<th>Oily phase [mL]</th>
<th>Water phase [mL]</th>
<th>Liquor [mL]</th>
<th>Pellet [mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>1.5</td>
<td>10.5</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>1.5</td>
<td>9.5</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>1</td>
<td>9</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 4.29: Volume of the sludge phases after compaction

Three phases are clearly visible after compaction of the sludge: oily phase (in average 8.9 %v/v), solid phase (the remaining pellets, in average 26.7 %v/v) and water phase (the supernatant, in average 64.4 %v/v). The moisture content $MC'$ of the pellet was 43.7 wt% and the dry matter ratio 56.3 wt%.
5.5.2. Freezing temperature -10°C, thawing temperature +20°C, 3 cycles

Freezing and thawing time
As in paragraph 5.4.2.

Frozen sample and leaching test
After three freezing cycles at -10°C, just before the beginning of the thawing phase, a tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. While extracting the solidified sludge, some oil that was in the top flowed away: the freezing temperature was not low enough to freeze it. In Figure 4.30 it is showed the frozen sample: the freezing cycles allow the solid material to settle in the bottom of the sludge; in the figure it is possible to distinguish quite clearly three frozen layers. The first layer is principally composed of floating material, trapped oil and gas bubbles produced by the bacterial activity while the sludge is thawed; the second layer is clear ice with dissolved material and the third layer is compacted sludge.

![Figure 4.30: Frozen sludge sample; a) top; b) side](image)

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.30.

<table>
<thead>
<tr>
<th>#</th>
<th>Mw [g]</th>
<th>Mb [g]</th>
<th>Ms [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.95</td>
<td>9.22</td>
<td>6.57</td>
<td>66.1</td>
<td>33.9</td>
<td>19.0</td>
<td>47.1</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>11.8</td>
<td>8.49</td>
<td>65.6</td>
<td>34.4</td>
<td>18.4</td>
<td>47.2</td>
</tr>
<tr>
<td>3</td>
<td>17.42</td>
<td>11.45</td>
<td>8.18</td>
<td>65.7</td>
<td>34.3</td>
<td>18.8</td>
<td>47.0</td>
</tr>
</tbody>
</table>

*Table 4.30: DR, OM, MC, MS of the treated sludge*
In average, DR = 65.8 wt% and MC = 34.2 wt%; OM = 18.7 wt% and Ms = 47.1 wt%, with a mass ratio OM:Ms equal to 1:2.51. 98 mL of leachate have been collected in the beaker; 1 subsample of 10 mL has been analysed; the results are shown in Table 4.31.

<table>
<thead>
<tr>
<th>#</th>
<th>Mw [g]</th>
<th>Md [g]</th>
<th>Ms [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.25</td>
<td>0.16</td>
<td>0.05</td>
<td>1.4</td>
<td>98.6</td>
<td>1.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 4.31: Characteristics of the leachate

The density of the leachate is equal to 994.3 g/L. The dry density $\rho_d$ is 16 g/L that means 1.6 g of dry material in 97 mL of leachate. No filter has been used in order to see if there are differences when it is used: when collected from the sieve, the leachate contains a thin layer of floating material that was trapped with the filter paper in the previous tests; in any case less than 2 grams of dry material were lost from the sieve. The plastic limit PL of the collected solid material over the sieve was 24.0 %.
5.5.3. Freezing temperature -20°C, thawing temperature +20°C, 3 cycles

Freezing and thawing time
As in paragraph 5.4.3.

Frozen sample and leaching test
After three freezing cycle at -20°C, just before the beginning of the thawing phase, a tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. While extracting, no liquor flowed away. Figure 4.31 shows the frozen sample: a subdivision of layers due to the cycles of freezing/thawing/settling should be visible, but the thin coating of frozen moisture makes it invisible. The top layer has a well visible spot of oil: the freezing treatment squeezes part of the oil that, during thawing, reaches the top layer; at -20°C the oil is really dense (or even frozen) and, because of that, it cannot flow away while the frozen sample is extracted from the tube.

![Figure 4.31: Frozen sludge sample; a) top; b) side](image)

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.32.

<table>
<thead>
<tr>
<th>#</th>
<th>M_W [g]</th>
<th>M_D [g]</th>
<th>M_S [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.77</td>
<td>11.04</td>
<td>7.81</td>
<td>65.8</td>
<td>34.2</td>
<td>19.3</td>
<td>46.6</td>
</tr>
<tr>
<td>2</td>
<td>13.52</td>
<td>8.87</td>
<td>6.25</td>
<td>65.6</td>
<td>34.4</td>
<td>19.4</td>
<td>46.2</td>
</tr>
<tr>
<td>3</td>
<td>17.89</td>
<td>11.75</td>
<td>8.18</td>
<td>65.7</td>
<td>34.3</td>
<td>20.0</td>
<td>45.7</td>
</tr>
</tbody>
</table>

Table 4.32: DR, OM, MC, MS of the treated sludge

In average, DR = 65.7 wt% and MC = 34.3 wt%; OM = 19.5 wt% and M_S = 46.2 wt%, with a mass ratio OM:M_S equal to 1:2.36. 104 mL of leachate have been collected in the beaker; 1 subsample of 10 mL has been analysed; the results are shown in Table 4.33.

<table>
<thead>
<tr>
<th>#</th>
<th>M_W [g]</th>
<th>M_D [g]</th>
<th>M_S [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.62</td>
<td>0.15</td>
<td>0.06</td>
<td>1.6</td>
<td>98.4</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 4.33: Characteristics of the leachate

The density of the leachate is equal to 994.5 g/L. The dry density ρ_d is 15 g/L that means 1.6 g of dry material in 104 mL of leachate. Less than 2 grams of dry material were lost from the sieve. The plastic limit PL of the collected solid material over the sieve was 24.3 %.
5.5.4. Freezing temperature -28°C, thawing temperature +20°C, 3 cycles

_Freezing and thawing time_
As in paragraph 5.4.4.

_Frozen sample and leaching test_
After three freezing cycles at the minimum temperature reachable by the freezer, just before the beginning of the thawing phase, a tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. No liquor flowed away while extracting the solidified sludge: the oil and the water are completely frozen. In Figure 4.32 is showed the frozen sample: the freezing cycles allowed the sedimentation of the suspended solids, thus the division in layers, although it is hard to see. The top of the frozen cylinder is lighter than the side, due to the presence of floating frozen oil; the cylinder is divided into two layers: the first layer is clarified water; the latter is compacted frozen sludge.

![Figure 4.32: Frozen sludge sample; a) top; b) side](image)

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.34.

<table>
<thead>
<tr>
<th>#</th>
<th>M_W [g]</th>
<th>M_D [g]</th>
<th>M_S [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.08</td>
<td>11.8</td>
<td>8.5</td>
<td>65.3</td>
<td>34.7</td>
<td>18.3</td>
<td>47.0</td>
</tr>
<tr>
<td>2</td>
<td>13.67</td>
<td>8.87</td>
<td>6.37</td>
<td>64.9</td>
<td>35.1</td>
<td>18.3</td>
<td>46.6</td>
</tr>
<tr>
<td>3</td>
<td>14.02</td>
<td>9.06</td>
<td>6.45</td>
<td>64.6</td>
<td>35.4</td>
<td>18.6</td>
<td>46.0</td>
</tr>
</tbody>
</table>

_Table 4.34: DR, OM, MC, MS of the treated sludge_

In average, DR = 64.9 wt% and MC = 35.1 wt%; OM = 18.4 wt% and M_S = 46.5 wt%, with a mass ratio OM:M_S equal to 1:2.53. 93 mL of leachate have been collected in the beaker; one subsample of 10 mL has been analysed; the results are shown in Table 4.35.
Table 4.35: Characteristics of the leachate

<table>
<thead>
<tr>
<th>#</th>
<th>( M_w ) [g]</th>
<th>( M_d ) [g]</th>
<th>( M_s ) [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.99</td>
<td>0.12</td>
<td>0.06</td>
<td>1.3</td>
<td>98.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

The density of the leachate is equal to 998.0 g/L, like the one of the water; the dry density \( \rho_d \) is 12 g/L that means 1.1 g of dry material in 93 mL of leachate. The filter has collected 0.3 g of dry material (oil and suspended solids). Less than 2 grams of dry material were lost from the sieve. The plastic limit PL of the collected solid material over the sieve was 25.0 \%. 


5.5.5. Comparison between the “3 cycles” tests

The following section will compare the experiments performed at different freezing temperatures with three freezing cycles. The freezing and thawing time comparison is the same of the one described in the paragraph 5.4.5: the time seems to be influenced only by the freezing temperature; there is not a relevant variation in freezing and thawing time of the sludge if one or three freezing cycles are performed.

**Compaction test**

The sludge appears not to be influenced by the freezing treatment; the compaction test has been performed on the untreated sludge (to have also more information about its composition) and on the sludge treated with three cycles of freeze at -5°C. The results are shown in Table 4.36:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture content of the pellet [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated sludge</td>
<td>39.8</td>
</tr>
<tr>
<td>Freezing temperature -5°C, thawing temperature +20°C, 3 cycles</td>
<td>43.7</td>
</tr>
</tbody>
</table>

Table 4.36: Pellets moisture content

The moisture content of the pellet collected from the compaction of the treated sludge should be inferior to the one of the untreated sludge. This discrepancy could be caused by the mixing of the treated sludge prior of its placement in the centrifuge tubes; this mixing can cause the rupture of the newly formed structures in the treated sludge and thus nullify the compaction test. For this reason no other compaction tests have been performed for the “3 cycles” tests.

**Leaching test**

The characteristics of the treated sludges obtained through the leaching test are compared in this paragraph; moisture content, dry matter ratio, organic matter and inorganic matter are shown and compared with the characteristics of the untreated sludge.

- **Moisture content:** The moisture content of the untreated sludge is compared with those of the treated sludges. The following table (Table 4.37) resumes the results shown before:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Freezing temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated sludge</td>
<td>-5</td>
</tr>
<tr>
<td>Moisture content [wt%]</td>
<td>60.6</td>
</tr>
</tbody>
</table>

Table 4.37: Moisture content of the untreated sludge and the leached sludges

Figure 4.33 plots the data shown above; the red line represents the moisture content of the untreated sludge, while the blue line represents the variation of moisture content in the leached sludge treated at different freezing temperatures.
The final product of the leaching test after 24 hours is a soil-like material with lower moisture content than the untreated sludge: the original sludge loses more or less 65% of its water content after freezing and thawing over a permeable stratum, no matter which freezing temperatures have been used. The lowest water content is reached with the treatment at -10 °C, while the highest at -28 °C.

**Composition of the dry content ratio**

The dry matter is composed of organic material, inorganic solids and oil. After the leaching, part of the oil flows away and also part of the dissolved solids; the amount of these losses depends on the freezing treatment at which the sludge has been subjected. The collected dry material over the sieve varies from freezing condition to freezing condition; in the following table (Table 4.38) the dry content ratios (DR) are resumed:

<table>
<thead>
<tr>
<th>Treating temperature [°C]</th>
<th>Collected material over the sieve [g]</th>
<th>DR [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5</td>
<td>205.8</td>
<td>64.5</td>
<td>19.3</td>
<td>45.2</td>
</tr>
<tr>
<td>-10</td>
<td>206.2</td>
<td>65.8</td>
<td>18.7</td>
<td>47.1</td>
</tr>
<tr>
<td>-20</td>
<td>209.4</td>
<td>65.7</td>
<td>19.5</td>
<td>46.2</td>
</tr>
<tr>
<td>-28</td>
<td>222.2</td>
<td>64.9</td>
<td>18.4</td>
<td>46.5</td>
</tr>
</tbody>
</table>

*Table 4.38: Composition of the dry matter*

The following graph (Figure 4.34) plots the data discussed above:
The gravimetric content ratios (wt\%) are converted in masses and compared below. The total mass of the collected samples (M_t) over the sieve is shown in Table 4.38; the mass of the untreated sample (M_U) of sludge in the tube is given by the product between the sludge density (\(\rho\)) and the tube volume (V_T):

\[ M_U = \rho \cdot V_T = 1152 \frac{g}{L} \cdot 0.300L = 345.6g \]

Figure 4.35 shows the composition of the untreated and treated sludges:

![Figure 4.35: Comparison between the untreated and the treated sludges](image)

The discussion regarding the water content has been already done in the previous paragraph. It is not wrong to consider that all the inorganic material M_S is trapped over the sieve and that the liquor is the only thing that passes it. Very little organic...
matter flows through the sieve: the oil seems to stay trapped inside the zots and the inorganic solids.

- **Plastic limit**
  The plastic limit comparison should show if different freezing temperatures produce an eventual modification of the solid structure of the treated sludge. In the next table (Table 4.39) are resumed the plastic limits PL found in each test:

<table>
<thead>
<tr>
<th>Test</th>
<th>Plastic limit [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freezing temperature -5°C, thawing temperature +20°C, 3 cycles</td>
<td>25.2</td>
</tr>
<tr>
<td>Freezing temperature -10°C, thawing temperature +20°C, 3 cycles</td>
<td>24</td>
</tr>
<tr>
<td>Freezing temperature -20°C, thawing temperature +20°C, 3 cycles</td>
<td>24.3</td>
</tr>
<tr>
<td>Freezing temperature -28°C, thawing temperature +20°C, 3 cycles</td>
<td>25</td>
</tr>
</tbody>
</table>

*Table 4.39: Plastic limits of the treated and leached sludges*

The results show that a clear modification of the sludge structure has not occurred when changing the freezing temperature of the treatment. The following graph (Figure 4.36) better clarifies what has been stated before:

The plastic limit can be considered constant, with an average of 24.6 wt%.
5.5.6. Freezing temperature -10°C, thawing temperature +20°C, 5 cycles

Freezing and thawing time
As in paragraph 5.4.2.

Frozen sample and leaching test
After five freezing cycles at -10°C, just before the beginning of the thawing phase, a tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. While extracting the solidified sludge, a good amount of oil that was in the top flowed away: the freezing temperature was not lower enough to freeze it. In Figure 4.37 it is showed the frozen sample: the freezing cycles allow the solid material to settle in the bottom of the sludge; in the figure it is possible to distinguish clearly the three frozen layers. The first layer is principally composed of floating material, trapped oil and gas bubbles produced by the bacterial activity while the sludge is thawed; the second layer is clear ice with dissolved material and the third layer is compacted sludge.

![Figure 4.37: Frozen sludge sample; a) top; b) side](image)

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.40.

<table>
<thead>
<tr>
<th>#</th>
<th>M_w [g]</th>
<th>M_0 [g]</th>
<th>M_s [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.66</td>
<td>10.64</td>
<td>7.64</td>
<td>67.9</td>
<td>32.1</td>
<td>19.2</td>
<td>48.8</td>
</tr>
<tr>
<td>2</td>
<td>11.62</td>
<td>7.9</td>
<td>5.71</td>
<td>68.0</td>
<td>32.0</td>
<td>18.8</td>
<td>49.1</td>
</tr>
<tr>
<td>3</td>
<td>18.94</td>
<td>12.77</td>
<td>9.12</td>
<td>67.4</td>
<td>32.6</td>
<td>19.3</td>
<td>48.2</td>
</tr>
</tbody>
</table>

Table 4.40: DR, OM, MC, MS of the treated sludge
In average, DR = 67.8 wt% and MC = 32.2 wt%; OM = 19.1 wt% and MS = 48.7 wt%, with a mass ratio OM:MS equal to 1:2.55. 96 mL of leachate have been collected in the beaker; 1 subsample of 10 mL has been analysed; the results are shown in Table 4.41.

<table>
<thead>
<tr>
<th>#</th>
<th>MW [g]</th>
<th>MD [g]</th>
<th>MS [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>MS [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.73</td>
<td>0.17</td>
<td>0.06</td>
<td>1.7</td>
<td>98.3</td>
<td>1.1</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 4.41: Characteristics of the leachate

The density of the leachate is equal to 998.4 g/L. The dry density $\rho_d$ is 17 g/L that means 1.6 g of dry material in 96 mL of leachate. No filter has been used in order to see if there are differences when it is used: when collected from the sieve, the leachate has a thin layer of floating material that was trapped with the filter paper in the previous tests; in any case less than 2 grams of dry material were lost from the sieve. The plastic limit PL of the collected solid material over the sieve was 23.7%.
5.5.7. Freezing temperature -20°C, thawing temperature +20°C, 5 cycles

Freezing and thawing time
As in paragraph 5.4.3.

Frozen sample and leaching test
After three freezing cycle at -20°C, just before the beginning of the thawing phase, a tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. While extracting, no liquor flowed away. Figure 4.38 shows the frozen sample: the subdivision of layers due to the cycles of freezing/thawing/settling is hardly visible. The top layer has a well visible spot of oil: the freezing treatment squeezes part of the oil that, during thawing, reaches the top layer; at -20°C the oil is really dense (or even frozen) and because of that it cannot flow away while the frozen sample is extracted from the tube.

![Figure 4.38: Frozen sludge sample; a) top; b) side](image)

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.42.

<table>
<thead>
<tr>
<th>#</th>
<th>M_W [g]</th>
<th>M_0 [g]</th>
<th>M_S [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.45</td>
<td>12.47</td>
<td>8.82</td>
<td>67.6</td>
<td>32.4</td>
<td>19.8</td>
<td>47.8</td>
</tr>
<tr>
<td>2</td>
<td>13.86</td>
<td>9.44</td>
<td>6.73</td>
<td>68.1</td>
<td>31.9</td>
<td>19.6</td>
<td>48.6</td>
</tr>
<tr>
<td>3</td>
<td>22.09</td>
<td>15.16</td>
<td>10.78</td>
<td>68.6</td>
<td>31.4</td>
<td>19.8</td>
<td>48.8</td>
</tr>
</tbody>
</table>

Table 4.42: DR, OM, MC, MS of the treated sludge
In average, DR = 68.1 wt% and MC = 31.9 wt%; OM = 19.7 wt% and Ms = 48.4 wt%, with a mass ratio OM:Ms equal to 1:2.45. 105 mL of leachate have been collected in the beaker; 1 subsample of 10 mL has been analysed; the results are shown in Table 4.43.

<table>
<thead>
<tr>
<th>#</th>
<th>M_w [g]</th>
<th>M_o [g]</th>
<th>M_s [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.71</td>
<td>0.17</td>
<td>0.07</td>
<td>1.8</td>
<td>98.2</td>
<td>1.0</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 4.43: Characteristics of the leachate

The density of the leachate is equal to 998.6 g/L; the dry density \( \rho_d \) is 17 g/L that means 1.8 g of dry material in 105 mL of leachate. Less than 2 grams of dry material were lost from the sieve. The plastic limit PL of the collected solid material over the sieve was 24.5 %.
5.5.8. Comparison between the “5 cycles” tests

This section compares the experiments performed at different freezing temperatures with five freezing cycles. The freezing and thawing time comparison is the same of the one described in the paragraph 5.4.5: the time seems to be influenced only by the freezing temperature; there is not a relevant variation in freezing and thawing time of the sludge if it is subjected to one, three or five freezing cycles. It has been decided to perform only two tests with five cycles (at -10 and -20°C) due to the long time that is needed to perform these experiments and in the light of the previous results: it has been thought that performing all the experiments was a waste of time, since the sludge seemed not to be influenced by the change of freezing temperature. -10°C and -20°C were chosen to be the proper temperatures with which freeze the samples, indeed, as stated in the paragraph 5.4.5, the range between these temperatures is the optimal condition at which perform the experiments.

Leaching test

No compaction test has been performed due to its ineffectiveness. The characteristics of the treated sludges obtained through the leaching test are compared in this paragraph; moisture content, dry matter ratio, organic matter and inorganic matter are shown and compared with the characteristics of the untreated sludge.

- Moisture content:

The moisture content of the untreated sludge is compared with those of the treated sludges. The following table (Table 4.44) resumes the results shown before:

<table>
<thead>
<tr>
<th>Moisture content [wt%]</th>
<th>Freezing temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated sludge</td>
<td>-5</td>
</tr>
<tr>
<td>60.6</td>
<td>/</td>
</tr>
</tbody>
</table>

Figure 4.39 plots the data shown above; the red line represents the moisture content of the untreated sludge, while the blue line represents the variation of moisture content in the leached sludge treated at different freezing temperatures. The final product of the leaching test after 24 hours is a soil-like material with lower moisture content than the untreated sludge: the original sludge looses more or less 68% of its water content after freezing and thawing over a permeable stratum, no matter which freezing temperatures have been used.
Composition of the dry content ratio

The dry matter is composed of organic material, inorganic solids and oil. After leaching, part of the oil flows away and also part of the dissolved solids; the amount of these losses depends on the freezing treatment at which the sludge has been subjected. The collected dry material over the sieve varies from freezing condition to freezing condition; in the following table (Table 4.45) the dry content ratios (DR) are resumed:

<table>
<thead>
<tr>
<th>Treating temperature [°C]</th>
<th>Collected material over the sieve [g]</th>
<th>DR [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>-10</td>
<td>210.1</td>
<td>67.8</td>
<td>19.1</td>
<td>48.7</td>
</tr>
<tr>
<td>-20</td>
<td>210.7</td>
<td>68.1</td>
<td>19.7</td>
<td>48.4</td>
</tr>
<tr>
<td>-28</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 4.45: Composition of the dry matter

The following graph (Figure 4.40) plots the data discussed above:
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Figure 4.40: Gravimetric content of the final product after leaching

The gravimetric content ratios (wt%) are converted in masses and compared with the untreated sludge properties. The total mass of the collected samples ($M_t$) over the sieve is shown in Table 4.45; the mass of the untreated sample ($M_U$) of sludge in the tube is given by the product between the sludge density ($\rho$) and the tube volume ($V_T$):

$$M_U = \rho \cdot V_T = 1152 \frac{g}{L} \cdot 0.300L = 345.6g$$

Figure 4.41 shows the composition of the untreated and treated sludges:

The discussion regarding the water content has been already done in the previous paragraph. It is not wrong to consider that all the inorganic material $M_S$ is trapped over the sieve and that the liquor is the only thing that passes it. Very little organic
matter flows through the sieve: the oil seems to stay trapped inside the zots and the inorganic solids.

- **Plastic limit**

In the next table (Table 4.46) are resumed the plastic limits PL found in each test:

<table>
<thead>
<tr>
<th>Test</th>
<th>Plastic limit [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freezing temperature -5°C, thawing temperature +20°C, 5 cycles</td>
<td>/</td>
</tr>
<tr>
<td>Freezing temperature -10°C, thawing temperature +20°C, 5 cycles</td>
<td>23.7</td>
</tr>
<tr>
<td>Freezing temperature -20°C, thawing temperature +20°C, 5 cycles</td>
<td>24.5</td>
</tr>
<tr>
<td>Freezing temperature -28°C, thawing temperature +20°C, 5 cycles</td>
<td>/</td>
</tr>
</tbody>
</table>

*Table 4.46: Plastic limits of the treated and leached sludges*

The results show that a clear modification of the sludge structure has not occurred when changing the freezing temperature of the treatment. The following graph (Figure 4.42) better clarifies what has been stated before:

The plastic limit can be considered constant, with an average of 24.1 wt%.
5.6. Sludge 1 - General comparison

A general comparison between the previous tests can now be done. In the previous paragraphs the differences between the treatments at different temperatures have been exposed in detail: the first conclusion is that the freezing temperature doesn’t influence the water and oil losses of the first sludge due to its particle size distribution; the very presence of oil can be an inhibitor factor of the freezing temperature effect. In this section a complete comparison of the results obtained using one, three or five freezing cycles will be done, to see if the freezing cycles have any kind of influences on the properties of the treated sludge. The leaching test has been performed for every freezing condition and, for this reason, only the results obtained with this procedure will be compared. The first graph (Figure 4.43) resumes the moisture contents found in the previous experiments, dividing them into groups depending on the number of freezing cycles. The moisture content decreases gradually with the increase of freezing cycles. Each freezing cycle leads to an increment in the compaction rate of the solids structure of the sludge do to the high presence of fine-grained particles in the material that makes the sludge slight frost susceptible; for this reason the water percentage is lower after thawing, but the difference is still negligible. Since the difference in moisture content is minimal, it is inadvisable to perform more than one cycle of treatment for this kind of sludge; otherwise the treatment cost will increase significantly.

![Figure 4.43: Leaching test - moisture content comparison](image)

This conclusion is reinforced by the fact that the organic content remains unchanged during all the experiments (see Figure 4.44): this means that the quantity of oil and dissolved organics that flow through the sieve is always the same, independently to the number of freezing cycles and freezing temperature with which the sludge was treated.
In order to figure out the losses of organic material (oil and dissolved organic matter) from the untreated sludge it is possible to compare the ratio OM/M_S of this one with the OM/M_S ratios of every treated sample; since a negligible quantity of solids pass through the 1 mm sieve, M_S can be considered always constant and the ratio OM/M_S is representative of the quantity of organic material that is trapped in the solid material over the sieve. Figure 4.45 shows schematically these ratios; it is immediately clear that the losses of organic material are insignificant. As already stated, the structure of the solid components of the sludge is changed, becoming more compact and increasing its porosity; this slight change is also visible analysing the values of the plastic limits found previously (Figure 4.46): after one freezing cycle the solid material can contain more water than the material treated with more cycles, this because each cycle increases the permeability of the material. There are no evident differences between the structures of the materials treated with 3 or 5 cycles. The influence of oil on the plastic limits is not well known.
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Figure 4.45: Leaching test – OM:M_s comparison

Figure 4.46: Leaching test – plastic limit comparison
5.7. Sludge 2 - Characterization

Thanks to the knowledge acquired analysing the first sludge, it has been possible to choose immediately the correct experiments to perform on the second sludge, without losing precious time. On prior analyses, the new sludge has lower water content than the first, and a behaviour that seems more similar to that of a soil instead of that of a wastewater sludge. Because of the high density of the sludge, it is not recommended to perform particular kind of analyses, like filtration over a filtering apparatus. The high density doesn’t allow performing the experiment to find the sludge volume index; the sludge has more the appearance of a saturated soil, but the presence of oil and other polluting substances forces us keeping distances to the term soil.

**pH, electroconductivity**

The previous experiments have shown how the electroconductivity of the untreated sludge is useless for its characterization, and even more in the comparison with the treated sludges. For this reason it has been considered a waste of time and material the analysis of the conductivity. The same can be said for the pH.

**Density, moisture and dry ratio**

The mass density of the sludge is equal to 1543 g/L. To measure moisture and dry ratio, different subsamples have been prepared, in order to have a more uniform result and eliminate the errors due to the presence of extraneous objects in the sludge. The next table (Table 4.47) shows the moisture content ratio and the dry ratio obtained for the sludge:

<table>
<thead>
<tr>
<th>Sub-sample</th>
<th>M_w [g]</th>
<th>M_D [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.71</td>
<td>13.71</td>
<td>66.2</td>
<td>33.8</td>
</tr>
<tr>
<td>2</td>
<td>24.34</td>
<td>15.84</td>
<td>65.1</td>
<td>34.9</td>
</tr>
<tr>
<td>3</td>
<td>25.16</td>
<td>16.13</td>
<td>64.1</td>
<td>35.9</td>
</tr>
<tr>
<td>4</td>
<td>13.61</td>
<td>8.9</td>
<td>65.4</td>
<td>34.6</td>
</tr>
</tbody>
</table>

*Table 4.47: Moisture and dry ratio*

The average DR is 65.2 wt% while the average MC is 34.8 wt%. The measured dry density (ρ_D) is equal to 1006 g/L. The volumetric percentage of water in the sludge is 53.7%.

**Volatile solids content**

After ignition, the volatile solids of the sludge (equal to the organic content composed by oil and organic matter) have been calculated, as showed in Table 4.48:

<table>
<thead>
<tr>
<th>Sub-sample</th>
<th>M_w [g]</th>
<th>M_D [g]</th>
<th>M_s [g]</th>
<th>OM [wt%]</th>
<th>M_s [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.71</td>
<td>13.71</td>
<td>11.49</td>
<td>10.7</td>
<td>55.5</td>
</tr>
<tr>
<td>2</td>
<td>24.34</td>
<td>15.84</td>
<td>13.24</td>
<td>10.7</td>
<td>54.4</td>
</tr>
<tr>
<td>3</td>
<td>25.16</td>
<td>16.13</td>
<td>13.28</td>
<td>11.3</td>
<td>52.8</td>
</tr>
<tr>
<td>4</td>
<td>13.61</td>
<td>8.9</td>
<td>7.49</td>
<td>10.4</td>
<td>55.0</td>
</tr>
</tbody>
</table>

*Table 4.48: Volatile solid content*

The average organic matter (OM) in the sludge is equal to 10.8 wt% while the inorganic solid content, in average, is 54.4 wt%. The sum of organic matter (OM) and inorganic solids (Ms) represents the dry ratio (DR) of the sludge. A schematic representation of the sludge composition is shown in Figure 4.47.
The percentages of organic matter and inorganic solids in the dry ratio are 16.3 wt% and 83.7 wt% respectively. The sludge is composed by 54% in volume of water.

Grain size distribution

The material has been cleaned as described in Chapter 4, paragraph 4.3.3. The resulting dry material is a grey mixture of particles. 48.42 grams of material have been analysed.

- Particle size distribution of coarse-grained material

A total mass of 29.11 g of material have been retained over all the sieves, that means that there are 19.31 g of material finer than 0.063 mm, equivalent to the 39.9 % of the total. Table 4.49 contains all the data collected from the sieving of the coarse-grained material:

<table>
<thead>
<tr>
<th>Sieve diameter [mm]</th>
<th>Retained on i-th sieve [g]</th>
<th>% Retained on i-th sieve</th>
<th>% Cumulative mass greater than i-th sieve</th>
<th>% Cumulative mass finer than i-th sieve</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6.18</td>
<td>21.2</td>
<td>21.2</td>
<td>78.8</td>
</tr>
<tr>
<td>1</td>
<td>3.19</td>
<td>11.0</td>
<td>32.2</td>
<td>67.8</td>
</tr>
<tr>
<td>0.5</td>
<td>5.78</td>
<td>19.9</td>
<td>52.0</td>
<td>48.0</td>
</tr>
<tr>
<td>0.25</td>
<td>7.72</td>
<td>26.5</td>
<td>78.6</td>
<td>21.4</td>
</tr>
<tr>
<td>0.125</td>
<td>5.15</td>
<td>17.7</td>
<td>96.3</td>
<td>3.7</td>
</tr>
<tr>
<td>0.063</td>
<td>1.09</td>
<td>3.7</td>
<td>100.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 4.49: Sieving analyses

From these data it is possible to draw the histogram of the granulometry (Figure 4.48) and the grain-size distribution curves (Figure 4.49) for the studied material.
• **Particle size distribution of fine-grained material**

The 39.9% of the initial material passed through the 0.063 mm sieve. Thanks to sedigraph measurements it has been possible to find directly the granulometry of this material. Figure 4.50 shows the histogram of the granulometry (mass frequency) while Figure 4.51 represents the grain-size distribution curve.
As it is possible to see in the two previous graphs, the measurements are not perfectly reliable. While performing the sedigraph measurements, the material didn’t wet properly in water, resulting in some errors. The complete analyses performed on the material with the particles diameter inferior than 0.063 mm is described in APPENDIX B.
5.8. Sludge 2 - External conditions that influence the sludge consolidation: variation of temperature

5.8.1. Freezing temperature -5°C, thawing temperature +20°C, 1 cycle

Freezing and thawing time
Two sludge tubes have been prepared; this time, because of the high density of the sludge, a spoon has been used for the preparation of the sample; the tube has been shaken several times in order to avoid air bubbles inside it. A temperature probe has been inserted in one of the tubes to register the freezing and thawing time; the other tube has been used to perform the leaching tests. The tubes have been placed in the freezer at a temperature of -5°C. After a freezing cycle, the tube with the probe has been placed outside at room temperature (+23°C) to register the thawing time. Figure 4.52 shows the freezing and thawing time (T5) proper to this sludge. The sludge needs 5 hours to freeze totally, plus other 2 hours and a half to reach the temperature of -5°C. When extracted from the freezer, the sludge in the tube needs 1 hour and a quarter to be totally thawed, plus other four hours to reach the room temperature. The probe inserted in the sludge is not perfectly calibrated; in fact it has a reading error of -1°C. In this circumstance, the sample starts freezing and thawing at 0°C.

Frozen sample and leaching test
After one freezing cycle, just before the beginning of the thawing phase, one of the two sample tubes (the one without temperature probe) has been placed out of the freezer. The sludge contained in the tube was extracted and placed over the sieve of the leaching apparatus. While extracting the frozen sludge, no liquor flowed away, like if it was totally dry. Figure 4.53 contains the pictures of the sludge (top and side) taken immediately after the
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...there is no phases subdivision because the sludge is too dense to show a solid precipitation in the short period of time before freezing.

![Figure 4.53: Frozen sludge sample; a) top; b) side](image)

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 2 subsamples have been analysed. The results are shown in Table 4.50.

<table>
<thead>
<tr>
<th>#</th>
<th>M_w [g]</th>
<th>M_D [g]</th>
<th>M_s [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.38</td>
<td>12.37</td>
<td>10.24</td>
<td>75.5</td>
<td>24.5</td>
<td>13.0</td>
<td>62.5</td>
</tr>
<tr>
<td>2</td>
<td>22.01</td>
<td>16.87</td>
<td>14.08</td>
<td>76.6</td>
<td>23.4</td>
<td>12.7</td>
<td>64.0</td>
</tr>
<tr>
<td>3</td>
<td>23.97</td>
<td>18.12</td>
<td>15.14</td>
<td>75.6</td>
<td>24.4</td>
<td>12.4</td>
<td>63.2</td>
</tr>
</tbody>
</table>

Table 4.50: DR, OM, MC, MS of the treated sludge

In average, DR = 75.9 wt% and MC = 24.1 wt%; OM = 12.7 wt% and Ms = 63.2 wt%, with a mass ratio OM:Ms equal to 1:4.98. 28 mL of leachate have been collected in the beaker; the collected liquor has been analysed; the results are shown in Table 4.51.

<table>
<thead>
<tr>
<th>#</th>
<th>M_w [g]</th>
<th>M_D [g]</th>
<th>M_s [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.62</td>
<td>0.02</td>
<td>0.02</td>
<td>0.3</td>
<td>99.7</td>
<td>0.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 4.51: Characteristics of the leachate

The plastic limit PL of the collected solid material over the sieve was 18.5 wt%.
5.8.2. Freezing temperature -10°C, thawing temperature +20°C, 1 cycle

Freezing and thawing time
Two sludge tubes have been prepared as described in the previous paragraph; a temperature probe has been inserted in one of the tubes to register the freezing and thawing time; the other tube has been used to perform the leaching tests. The tubes have been placed in the freezer at a temperature of -10°C. After a freezing cycle, the tube with the probe has been placed outside at room temperature (+23°C) to register the thawing time. Figure 4.54 shows the freezing and thawing time (T5) proper to this sludge. The sludge needs 3 hours and a half to freeze totally, plus other 2 hours and a half to reach the temperature of -10°C. When extracted from the freezer, the sludge in the tube needs 3 hours to be totally thawed, plus other four hours and a half to reach the room temperature. The probe inserted in the sludge is not perfectly calibrated; in fact it has a reading error of -1°C; the sample starts freezing and thawing at 0°C.

Frozen sample and leaching test
After one freezing cycle, just before the beginning of the thawing phase, one of the two sample tubes (the one without temperature probe) has been placed out of the freezer. The sludge contained in the tube was extracted and placed over the sieve of the leaching apparatus. While extracting the frozen sludge, no liquor flowed away, like if it was totally dry. Figure 4.55 contains the pictures of the sludge (top and side) taken immediately after the extraction; there is no phases subdivision because the sludge is too dense to show a solid precipitation in the short period of time before freezing.
After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 2 subsamples have been analysed. The results are shown in Table 4.52.

<table>
<thead>
<tr>
<th>#</th>
<th>( M_W ) [g]</th>
<th>( M_0 ) [g]</th>
<th>( M_S ) [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.91</td>
<td>14.3</td>
<td>11.85</td>
<td>71.8</td>
<td>28.2</td>
<td>12.3</td>
<td>59.5</td>
</tr>
<tr>
<td>2</td>
<td>10.19</td>
<td>7.31</td>
<td>6.09</td>
<td>71.7</td>
<td>28.3</td>
<td>12.0</td>
<td>59.8</td>
</tr>
</tbody>
</table>

Table 4.52: DR, OM, MC, MS of the treated sludge

In average, \( DR = 71.8 \) wt% and \( MC = 28.2 \) wt%; \( OM = 12.1 \) wt% and \( MS = 59.6 \) wt%, with a mass ratio OM:MS equal to 1:4.91. Less than 10 mL of leachate have been collected in the beaker; the collected liquor has been analysed; the results are shown in Table 4.53.

<table>
<thead>
<tr>
<th>#</th>
<th>( M_W ) [g]</th>
<th>( M_0 ) [g]</th>
<th>( M_S ) [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.79</td>
<td>0.23</td>
<td>0.14</td>
<td>2.0</td>
<td>98.0</td>
<td>0.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 4.53: Characteristics of the leachate

The plastic limit PL of the collected solid material over the sieve was 18.7 wt%.
5.8.3. Freezing temperature -20°C, thawing temperature +20°C, 1 cycle

Freezing and thawing time
The graph that shows the freezing and thawing time is missing, but the required data have been registered: the freezing time was 100 min and the thawing time 215 min.

Frozen sample and leaching test
After one freezing cycle at -20°C, just before the beginning of the thawing phase, one sample tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. While extracting the solidified sludge no liquor flowed away due to the freezing temperature and the high density of the sludge. In Figure 4.56 is showed the frozen sample: the rapid freezing time didn’t let the suspended material to sediment, in fact the frozen sludge has a uniform black colour.

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.54.

<table>
<thead>
<tr>
<th>#</th>
<th>$M_w$ [g]</th>
<th>$M_0$ [g]</th>
<th>$M_s$ [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.64</td>
<td>16.33</td>
<td>13.54</td>
<td>72.1</td>
<td>27.9</td>
<td>12.3</td>
<td>59.8</td>
</tr>
<tr>
<td>2</td>
<td>17.06</td>
<td>12.36</td>
<td>10.35</td>
<td>72.5</td>
<td>27.5</td>
<td>11.8</td>
<td>60.7</td>
</tr>
<tr>
<td>3</td>
<td>48.11</td>
<td>34.54</td>
<td>28.68</td>
<td>71.8</td>
<td>28.2</td>
<td>12.2</td>
<td>59.6</td>
</tr>
</tbody>
</table>

Table 4.54: DR, OM, MC, MS of the treated sludge

In average, DR = 72.1 wt% and MC = 27.9 wt%; OM = 12.1 wt% and Ms = 60.0 wt%, with a mass ratio OM:Ms equal to 1:4.96. Less than 10 mL of leachate have been collected in the beaker; the collected liquor has been analysed; the results are shown in Table 4.55.

<table>
<thead>
<tr>
<th>#</th>
<th>$M_w$ [g]</th>
<th>$M_0$ [g]</th>
<th>$M_s$ [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.22</td>
<td>0.19</td>
<td>0.12</td>
<td>2.6</td>
<td>97.4</td>
<td>1.0</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 4.55: Characteristics of the leachate

The plastic limit PL of the collected solid material over the sieve was 18.5 wt%.
5.8.4. Freezing temperature -28°C, thawing temperature +20°C, 1 cycle

Freezing and thawing time
Two sludge tubes have been prepared as described previously; a temperature probe has been inserted in one of the tubes to register the freezing and thawing time; the other tube has been used to perform the leaching tests. The tubes have been placed in the freezer at a temperature of -28°C, the minimum temperature that the freezer can reach. After a freezing cycle, the tube with the probe has been placed outside at room temperature (+23°C) to register the thawing time. Figure 4.57 shows the freezing and thawing time (T2) proper to this sludge. The sludge needs one hour and a half to freeze totally, plus other 2 hours and to reach the temperature of -28°C. When extracted from the freezer, the sludge in the tube needs almost 4 hours to be totally thawed, plus other four hours to reach the room temperature. The probe inserted in the sludge is not perfectly calibrated; in fact it has a reading error of -1°C; the sample starts freezing and thawing at 0°C.

![Figure 4.57: Freezing and thawing time](image)

Frozen sample and leaching test
After one freezing cycle at -28°C, just before the beginning of the thawing phase, one sample tube was pulled out to the freezer; the frozen cylinder of sludge has been extracted from the tube and used to perform the leaching test. While extracting the solidified sludge no liquor flowed away due to the freezing temperature and the high density of the sludge. In Figure 4.58 is showed the frozen sample: the rapid freezing time didn’t let the suspended material to sediment, in fact the frozen sludge has a uniform colour.
After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.56.

<table>
<thead>
<tr>
<th>#</th>
<th>$M_W$ [g]</th>
<th>$M_D$ [g]</th>
<th>$M_S$ [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>MS [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.61</td>
<td>19.7</td>
<td>16.63</td>
<td>74.0</td>
<td>26.0</td>
<td>11.5</td>
<td>62.5</td>
</tr>
<tr>
<td>2</td>
<td>23.01</td>
<td>16.82</td>
<td>14.06</td>
<td>73.1</td>
<td>26.9</td>
<td>12.0</td>
<td>61.1</td>
</tr>
<tr>
<td>3</td>
<td>23.5</td>
<td>17.07</td>
<td>14.29</td>
<td>72.6</td>
<td>27.4</td>
<td>11.8</td>
<td>60.8</td>
</tr>
</tbody>
</table>

Table 4.56: DR, OM, MC, MS of the treated sludge

In average, DR = 73.3 wt% and MC = 26.7 wt%; OM = 11.8 wt% and MS = 61.5 wt%, with a mass ratio OM:MS equal to 1:5.21. 12 mL of leachate have been collected in the beaker; the collected liquor has been analysed; the results are shown in Table 4.57.

<table>
<thead>
<tr>
<th>#</th>
<th>$M_W$ [g]</th>
<th>$M_D$ [g]</th>
<th>$M_S$ [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>MS [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.1</td>
<td>0.13</td>
<td>0.05</td>
<td>1.1</td>
<td>98.9</td>
<td>0.7</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 4.57: Characteristics of the leachate

The plastic limit PL of the collected solid material over the sieve was 17.8 wt%.
5.8.5. Comparison

In this section all the previous experiments regarding the freezing treatment on the second sludge at different temperatures will be compared and discussed. The final goal of this comparison is to find the best condition with which it is better to treat the sludge to achieve the greater reduction in water and oil content after freezing and thawing.

**Freezing and thawing time**

The first comparison regards the freezing and thawing times of the sludges treated at different freezing temperatures. The tubes don’t represent correctly what happens in reality, but give a better knowledge on the necessary treatment time and, at the same time, on the treatment cost. A sludge treated at a lower temperature requires less time to be frozen, but more time to be completely thawed; this behaviour influences costs and time for the treatment of the sludge.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Freezing time [min]</th>
<th>Thawing time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5</td>
<td>294</td>
<td>78</td>
</tr>
<tr>
<td>-10</td>
<td>207</td>
<td>174</td>
</tr>
<tr>
<td>-20</td>
<td>100</td>
<td>215</td>
</tr>
<tr>
<td>-28</td>
<td>91</td>
<td>229</td>
</tr>
</tbody>
</table>

*Table 4.58: Freezing and thawing time*

The results can be compared in graphs, to have a better overview of the freezing phenomena (see Figure 4.59a and 4.59b).

![Freezing and Thawing Time Graphs](image)

*Figure X: a) Freezing time; b) Thawing time*

The total treatment time (freezing time plus thawing time) required is shown in Figure 4.60:
The total treatment time is between 5 and 6 hours.

**Leaching test**

The characteristics of the treated sludges obtained through the leaching test are compared in this paragraph; moisture content, dry matter ratio, organic matter and inorganic matter are shown and compared with the characteristics of the untreated sludge.

- **Moisture content:**
  The moisture content of the untreated sludge is compared with those of the treated sludges. The following table (Table 4.59) resumes the results shown before:

<table>
<thead>
<tr>
<th>Moisture content [wt%]</th>
<th>Freezing temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-treated sludge</td>
<td>-5</td>
</tr>
<tr>
<td>34.8</td>
<td>24.1</td>
</tr>
</tbody>
</table>

*Table 4.59: Moisture content of the untreated sludge and the leached sludges*

Figure 4.61 plots the data shown above; the red line represents the moisture content of the untreated sludge, while the blue line represents the variation of moisture content in the leached sludge treated at different freezing temperatures.
Chapter 5: Results and discussion

Figure 4.61: Moisture content

The final product of the leaching test after 24 hours is a soil-like material with lower moisture content than the untreated sludge: the original sludge loses more or less 33.1% of its water content after freezing and thawing over a permeable stratum. The lowest water content is reached with the treatment at -5 °C, while the highest at -10 °C; the difference is not so high. At -5°C the transformation of water into well formed ice crystals can have a stronger effect on the compaction of the material, increasing its porosity and the amount of water lost. The other temperatures don’t affect the moisture contents of the treated material.

- Composition of the dry content ratio

The dry matter is composed of organic material, inorganic solids and oil. After the leaching, part of the oil is supposed to flow away and also part of the dissolved solids; the amount of these losses depends on the freezing treatment at which the sludge has been subjected. Since the sludge has been pre-treated to remove some oil prior its arrival in the laboratory, probably this loss will be minimal. The collected dry material over the sieve varies from freezing condition to freezing condition; in the following table (Table 4.60) the dry content ratios (DR) are resumed:

<table>
<thead>
<tr>
<th>Treating temperature [°C]</th>
<th>Collected material over the sieve [g]</th>
<th>DR [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5</td>
<td>385.0</td>
<td>75.9</td>
<td>12.7</td>
<td>63.2</td>
</tr>
<tr>
<td>-10</td>
<td>402.5</td>
<td>71.8</td>
<td>12.1</td>
<td>59.6</td>
</tr>
<tr>
<td>-20</td>
<td>406.4</td>
<td>72.1</td>
<td>12.1</td>
<td>60</td>
</tr>
<tr>
<td>-28</td>
<td>417.0</td>
<td>73.3</td>
<td>11.8</td>
<td>61.5</td>
</tr>
</tbody>
</table>

Table 4.60: Composition of the dry matter

The following graph (Figure 4.62) plots the data shown above:
The tubes contain more or less 300 mL of sludge. In average, the weight of the untreated sludge is, therefore:

\[ M_U = \rho \cdot V_T = 1543 \frac{g}{L} \cdot 0.300L = 462.9 g \]

Figure 4.63 shows the composition of the untreated and treated sludges:

The discussion regarding the water content has been done in the previous paragraph. All the inorganic material Ms is trapped over the sieve; the liquor is the only thing that passes it. As thought before, no organic material flows through the sieve: the few remained oil after the pre-treatment stays trapped inside the zots and the inorganic solids.
• **Plastic limit**

The plastic limit comparison should show if different freezing temperatures produce an eventual modification of the solid skeleton of the treated sludge. The next table (Table 4.61) resumes the plastic limits PL found in each test:

<table>
<thead>
<tr>
<th>Test</th>
<th>Plastic limit [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freezing temperature -5°C, thawing temperature +20°C, 1 cycle</td>
<td>18.5</td>
</tr>
<tr>
<td>Freezing temperature -10°C, thawing temperature +20°C, 1 cycle</td>
<td>18.7</td>
</tr>
<tr>
<td>Freezing temperature -20°C, thawing temperature +20°C, 1 cycle</td>
<td>18.5</td>
</tr>
<tr>
<td>Freezing temperature -28°C, thawing temperature +20°C, 1 cycle</td>
<td>17.9</td>
</tr>
</tbody>
</table>

*Table 4.61: Plastic limits of the treated and leached sludges*

No significant change in the treated sludge appears from these data or from the relative graph (Figure 4.64):

The plastic limit can be considered constant, with an average of 18.4 wt%.
5.9. Sludge 2 - External conditions that influence the sludge consolidation: number of freezing/thawing cycles

5.9.1. Freezing temperature -5°C, thawing temperature +20°C, 3 cycles

Freezing and thawing time
As in paragraph 5.8.1.

Frozen sample and leaching test
After three freezing cycles, just before the beginning of the thawing phase, one sample tube has been placed out of the freezer. The frozen sludge contained in the tube was extracted and placed over the sieve of the leaching apparatus. While extracting the frozen sludge, no liquor flowed away, like if it was totally dry. Figure 4.65 contains the pictures of the sludge (top and side) taken immediately after the extraction; a phase subdivision is visible: a solid black phase and a frozen solution phase 5 mm thick. The cycles allow the sedimentation of the solid material although it is not as clear as in the first sludge.

![Figure 4.65: Frozen sludge sample; a) top; b) side](image)

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.62.

<table>
<thead>
<tr>
<th></th>
<th>MW [g]</th>
<th>MD [g]</th>
<th>MS [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.72</td>
<td>16.01</td>
<td>13.3</td>
<td>73.7</td>
<td>26.3</td>
<td>12.5</td>
<td>61.2</td>
</tr>
<tr>
<td>2</td>
<td>19.07</td>
<td>14.01</td>
<td>11.65</td>
<td>73.5</td>
<td>26.5</td>
<td>12.4</td>
<td>61.1</td>
</tr>
<tr>
<td>3</td>
<td>23.28</td>
<td>17.12</td>
<td>14.15</td>
<td>73.5</td>
<td>26.5</td>
<td>12.8</td>
<td>60.8</td>
</tr>
</tbody>
</table>

Table 4.62: DR, OM, MC, MS of the treated sludge
In average, DR = 73.6 wt% and MC = 26.4 wt%; OM = 12.5 wt% and Ms = 61.0 wt%, with a mass ratio OM:Ms equal to 1:4.87. 28 mL of leachate have been collected in the beaker; the collected liquor has been analysed; the results are shown in Table 4.63.

<table>
<thead>
<tr>
<th>#</th>
<th>Mw [g]</th>
<th>Mo [g]</th>
<th>Ms [g]</th>
<th>DR  [wt%]</th>
<th>MC  [wt%]</th>
<th>OM  [wt%]</th>
<th>Ms  [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.06</td>
<td>0.06</td>
<td>0.05</td>
<td>0.7</td>
<td>99.3</td>
<td>0.1</td>
<td>0.6</td>
</tr>
</tbody>
</table>

*Table 4.63: Characteristics of the leachate*

The plastic limit PL of the collected solid material over the sieve was 19.1 wt%.
5.9.2. Freezing temperature -10°C, thawing temperature +20°C, 3 cycles

**Freezing and thawing time**
As in paragraph 5.8.2.

**Frozen sample and leaching test**
After three freezing cycles, just before the beginning of the thawing phase, the sample tube has been placed out of the freezer. The frozen sludge contained in the tube was extracted and placed over the sieve of the leaching apparatus. While extracting the frozen sludge, no liquor flowed away, like if it was totally dry. Figure 4.66 contains the pictures of the sludge (top and side) taken immediately after the extraction; a phase subdivision is slightly visible. The cycles allow the sedimentation of the solid material although it is not as clear as in the first sludge.

![Figure 4.66: Frozen sludge sample; a) top; b) side](image)

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.64.

<table>
<thead>
<tr>
<th>#</th>
<th>$M_w$ [g]</th>
<th>$M_o$ [g]</th>
<th>$M_s$ [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.63</td>
<td>16.91</td>
<td>14.45</td>
<td>74.7</td>
<td>25.3</td>
<td>10.9</td>
<td>63.9</td>
</tr>
<tr>
<td>2</td>
<td>19.77</td>
<td>14.93</td>
<td>12.7</td>
<td>75.5</td>
<td>24.5</td>
<td>11.3</td>
<td>64.2</td>
</tr>
<tr>
<td>3</td>
<td>11.82</td>
<td>8.95</td>
<td>7.58</td>
<td>75.7</td>
<td>24.3</td>
<td>11.6</td>
<td>64.1</td>
</tr>
</tbody>
</table>

*Table 4.64: DR, OM, MC, MS of the treated sludge*

In average, DR = 75.3 wt% and MC = 24.7 wt%; OM = 11.2 wt% and $M_s$ = 64.1 wt%, with a mass ratio OM:$M_s$ equal to 1:5.70. No leachate has been collected in the beaker. The plastic limit PL of the collected solid material over the sieve was 18.3 wt%.
5.9.3. Freezing temperature -20°C, thawing temperature +20°C, 3 cycles

Freezing and thawing time
As in paragraph 5.8.3.

Frozen sample and leaching test
After three freezing cycles, just before the beginning of the thawing phase, one sample tube has been placed out of the freezer. The frozen sludge contained in the tube was extracted and placed over the sieve of the leaching apparatus. While extracting the frozen sludge, no liquor flowed away. Figure 4.67 contains the pictures of the sludge (top and side) taken immediately after the extraction; a phase subdivision is slightly visible: a solid black phase and a frozen solution phase 5 mm thick. The cycles allow the sedimentation of the solid material although it is not as clear as in the first sludge. In the sludge are also visible some ice intrusions.

![Figure 4.67: Frozen sludge sample; a) top; b) side](image)

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.65.

<table>
<thead>
<tr>
<th>#</th>
<th>M₀ [g]</th>
<th>M₀ [g]</th>
<th>Mₛ [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.14</td>
<td>17.03</td>
<td>14.21</td>
<td>73.6</td>
<td>26.4</td>
<td>12.2</td>
<td>61.4</td>
</tr>
<tr>
<td>2</td>
<td>21.74</td>
<td>16.29</td>
<td>13.64</td>
<td>74.9</td>
<td>25.1</td>
<td>12.2</td>
<td>62.7</td>
</tr>
<tr>
<td>3</td>
<td>29.05</td>
<td>21.75</td>
<td>18.22</td>
<td>74.9</td>
<td>25.1</td>
<td>12.2</td>
<td>62.7</td>
</tr>
</tbody>
</table>

Table 4.65: DR, OM, MC, MS of the treated sludge

In average, DR = 74.5 wt% and MC = 25.5 wt%; OM = 12.2 wt% and Ms = 62.3 wt%, with a mass ratio OM:Ms equal to 1:5.12. No leachate has been collected. The plastic limit PL of the collected solid material over the sieve was 18.5 wt%.
5.9.4. Freezing temperature -28°C, thawing temperature +20°C, 3 cycles

**Freezing and thawing time**
As in paragraph 5.8.4.

**Frozen sample and leaching test**
After three freezing cycles, just before the beginning of the thawing phase, one sample tube has been placed out of the freezer. The frozen sludge contained in the tube was extracted and placed over the sieve of the leaching apparatus. While extracting the frozen sludge, no liquor flowed away. Figure 4.68 contains the pictures of the sludge (top and side) taken immediately after the extraction; a phase subdivision is visible: a solid black phase and a frozen solution phase 5 mm thick. The cycles allow the sedimentation of the solid material although it is not as clear as in the first sludge.

![Figure 4.68: Frozen sludge sample; a) top; b) side](image)

After 24 hours of leaching, the solid material has been collected; after being mixed with a spoon, 3 subsamples have been analysed. The results are shown in Table 4.66.

<table>
<thead>
<tr>
<th>#</th>
<th>MW [g]</th>
<th>MD [g]</th>
<th>MS [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>MS [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.66</td>
<td>20.96</td>
<td>17.51</td>
<td>73.1</td>
<td>26.9</td>
<td>12.0</td>
<td>61.1</td>
</tr>
<tr>
<td>2</td>
<td>26.86</td>
<td>19.56</td>
<td>16.38</td>
<td>72.8</td>
<td>27.2</td>
<td>11.8</td>
<td>61.0</td>
</tr>
<tr>
<td>3</td>
<td>28.8</td>
<td>20.82</td>
<td>17.24</td>
<td>72.3</td>
<td>27.7</td>
<td>12.4</td>
<td>59.9</td>
</tr>
</tbody>
</table>

*Table 4.66: DR, OM, MC, MS of the treated sludge*

In average, DR = 72.7 wt% and MC = 27.3 wt%; OM = 12.1 wt% and MS = 60.6 wt%, with a mass ratio OM:MS equal to 1:5.01. 14 mL of leachate have been collected in the beaker; the collected liquor has been analysed; the results are shown in Table 4.67.

<table>
<thead>
<tr>
<th>#</th>
<th>MW [g]</th>
<th>MD [g]</th>
<th>MS [g]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>MS [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.07</td>
<td>0.22</td>
<td>0.13</td>
<td>1.8</td>
<td>98.2</td>
<td>0.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*Table 4.67: Characteristics of the leachate*

The plastic limit PL of the collected solid material over the sieve was 18.6wt%.
5.9.5. Comparison

In this section all the previous experiments regarding the freezing treatment on the second sludge at different temperatures with three cycles will be compared and discussed. The final goal of this comparison is to find the best condition with which treat the sludge to achieve the greater reduction in water and oil content after freezing and thawing. The freezing and thawing time comparison is the same of the one described in the paragraph 5.8.5: the time seems to be influenced only by the freezing temperature; there is not a relevant variation in freezing and thawing time of the sludge if it subjected to one or three cycles.

Leaching test

The characteristics of the treated sludges obtained through the leaching test are compared in this paragraph; moisture content, dry matter ratio, organic matter and inorganic matter are shown and compared with the characteristics of the untreated sludge.

- Moisture content:

The moisture content of the untreated sludge is compared with those of the treated sludges. The following table (Table 4.68) resumes the results shown before:

<table>
<thead>
<tr>
<th>Untreated sludge</th>
<th>Freezing temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content [wt%]</td>
<td>-5</td>
</tr>
<tr>
<td>34.8</td>
<td>26.4</td>
</tr>
</tbody>
</table>

Table 4.68: Moisture content of the untreated sludge and the leached sludges

Figure 4.69 plots the data shown above; the red line represents the moisture content of the untreated sludge, while the blue line represents the variation of moisture content in the leached sludge treated at different freezing temperatures.
The final product of the leaching test after 24 hours is a soil-like material with lower moisture content than the untreated sludge: the original sludge looses more or less 35.4 % of its water content after freezing and thawing over a permeable stratum. The lowest water content is reached with the treatment at -10 °C, while the highest at -5 °C, but the difference is not so high.

- **Composition of the dry content ratio**

  The dry matter is composed of organic material, inorganic solids and oil. After the leaching, part of the oil is supposed to flow away and also part of the dissolved solids; the amount of these losses depends on the freezing treatment at which the sludge has been subjected. Since the sludge has been pre-treated to remove some oil prior its arrival in the laboratory, probably this loss will be minimal. The collected dry material over the sieve varies from freezing condition to freezing condition; in the following table (Table 4.69) the dry content ratios (DR) are resumed:

<table>
<thead>
<tr>
<th>Treating temperature [°C]</th>
<th>Collected material over the sieve [g]</th>
<th>DR [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5</td>
<td>399.2</td>
<td>73.6</td>
<td>12.5</td>
<td>61</td>
</tr>
<tr>
<td>-10</td>
<td>387.4</td>
<td>75.3</td>
<td>11.2</td>
<td>64.1</td>
</tr>
<tr>
<td>-20</td>
<td>420.5</td>
<td>74.5</td>
<td>12.2</td>
<td>62.3</td>
</tr>
<tr>
<td>-28</td>
<td>396.9</td>
<td>72.7</td>
<td>12.1</td>
<td>60.6</td>
</tr>
</tbody>
</table>

*Table 4.69: Composition of the dry matter*

The following graph (Figure 4.70) plots the data discussed above:

![Graph](image)

*Figure 4.70: Gravimetric content of the final product after leaching*

The tubes contain more or less 300 mL of sludge. In average, the weight of the untreated sludge is, therefore:

\[
M_U = \rho \cdot V_T = 1543 \cdot \frac{g}{L} \cdot 0.300L = 462.9g
\]
Figure 4.71 shows the composition of the untreated and treated sludges:

![Figure 4.71: Comparison between the untreated and the treated sludges](image)

The discussion regarding the water content has been done in the previous paragraph. All the inorganic material $M_S$ is trapped over the sieve; the liquor is the only thing that passes it. As thought before, no organic material flows through the sieve: the few remained oil after the pre-treatment stays trapped inside the zots and the inorganic solids. The tube treated at -20°C was containing a bigger amount of sludge.

- **Plastic limit**
  The plastic limit comparison should show if different freezing temperatures produce an eventual modification of the solid skeleton of the treated sludge. In the next table (Table 4.70) are resumed the plastic limits PL found in each test:

<table>
<thead>
<tr>
<th>Test</th>
<th>Plastic limit [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freezing temperature -5°C, thawing temperature +20°C, 3 cycles</td>
<td>19.1</td>
</tr>
<tr>
<td>Freezing temperature -10°C, thawing temperature +20°C, 3 cycles</td>
<td>18.3</td>
</tr>
<tr>
<td>Freezing temperature -20°C, thawing temperature +20°C, 3 cycles</td>
<td>18.5</td>
</tr>
<tr>
<td>Freezing temperature -28°C, thawing temperature +20°C, 3 cycles</td>
<td>18.6</td>
</tr>
</tbody>
</table>

*Table 4.70: Plastic limits of the treated and leached sludges*

No significant change in the treated sludge appears from these data or from the relative graph (Figure 4.72):
The plastic limit can be considered constant, with an average of 18.6 wt%.
5.10. Sludge 2 - General comparison

From the previous comparisons it has been clear that the variation of freezing temperature seems not to influence the compaction of the second sludge or minimally. The moisture content changes slightly, while the organic matter is not influenced: since the sludge has been deprived of part of its oil there are no losses of it while thawing. The composition of the material, its grain size distribution and its oil content are the reasons why the variation of temperature doesn’t affect the water loss. In this section a complete comparison of the results obtained using one or three freezing cycles will be done, to see if the freezing cycles have any kind of influences on the properties of the treated sludge. Since the leaching test has been performed for every freezing condition, only the results obtained with this experiment will be compared. The first graph (Figure 4.73) resumes the moisture contents found in the previous experiments, dividing them in groups depending on the number of freezing cycles. The moisture content changes depending on the number of freezing cycles; with three freezing cycles the compaction is slightly more pronounced if the temperature is inferior of -7°C: this is due to the presence of fine grained material in the sludge; at -28°C the effect is no more visible, maybe due to an high freezing rate (formation of ice dendrites in the water while freezing) and a consequent reduction in compaction capacity. Since the difference in moisture content is minimal, it is inadvisable to perform more than one cycle of treatment for the second sludge; otherwise the treatment cost will increase significantly.

![Moisture content MC graph]

The organic content remains unchanged during all the experiments (see Figure 4.74): that means that the quantity of oil and dissolved organics that flow through the sieve is always the same, without being dependent to the number of freezing cycles and freezing temperature
with which the sludge was treated. The oil removal is not influenced by the freezing temperature, neither by the number of freezing/thawing cycles.

In order to figure out the losses of organic material (oil and dissolved organic matter) from the untreated sludge it is possible to compare the ratio OM/MS of this one with the OM/MS ratios of every treated sample; since a negligible quantity of solids pass through the 1 mm sieve, MS can be considered always constant and the ratio OM/MS is representative of the quantity of organic material that is trapped in the solid material over the sieve. Figure 4.75 shows schematically these ratios; it is immediately clear that the losses of organic material are insignificant. The plastic limits trend (Figure 4.76) is not affected by freezing temperature and number of cycles; there are no important structural changes in the material skeleton. The influence of oil on the plastic limits is not well known.
Chapter 5: Results and discussion

Figure 4.75: Leaching test – OM:MS comparison

Figure 4.76: Leaching test – plastic limit comparison
Chapter 5: Results and discussion

5.11. Comparison between the two sludges

The external freezing conditions and the internal characteristics of the sludge influence its behaviour while freezing and its compaction during thawing. In this section the different internal characteristics of the two sludges are compared in relation with the used external freezing conditions.

5.11.1. Untreated sludges

In this paragraph the characteristics of the untreated sludges will be compared. The sludges analysed in this essay came from the same workshop but, while the first was unaltered when sent to the laboratory, the second underwent several processes to remove part of its water and oil content. Table 4.71 resumes the principal characteristics that have been first analysed:

<table>
<thead>
<tr>
<th></th>
<th>Density [g/L]</th>
<th>DR [wt%]</th>
<th>MC [wt%]</th>
<th>OM [wt%]</th>
<th>Ms [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge 1 (S1)</td>
<td>1151.9</td>
<td>39.4</td>
<td>60.6</td>
<td>11.7</td>
<td>27.7</td>
</tr>
<tr>
<td>Sludge 2 (S2)</td>
<td>1542.9</td>
<td>65.2</td>
<td>34.8</td>
<td>10.8</td>
<td>54.4</td>
</tr>
</tbody>
</table>

Table 4.71: Sludge characteristics

A better comparison can be obtained plotting this data in a graph, as shown in Figure 4.77:

The moisture content of the first sludge is quite the double of the second and for this reason it has a liquid behaviour. The inorganic material is the principal component of the second sludge; moreover its OM/Ms ratio is much lower than the one of the first sludge: there is less organic material for all the inorganic solids; the remaining oil after the pre-treatment is therefore well bounded to the inorganic material and it doesn’t flow away in the leachate when the frozen sludge thaws. On the contrary, little oil was leached from the first sludge while thawing: the oil was squeezed out from the particles by the ice front, allowing it to flow during thawing. The moisture content that the studied sludges have after a cycle of freezing/thawing/leaching depends principally on their grain size distribution. The first sludge is principally fine-grained, while the second is mostly coarse-grained (Table 4.72), but it is the fine-grained material that influences the sludge behaviour.
Table 4.72: Percentage of passing and retained over the 0.064 mm sieve

<table>
<thead>
<tr>
<th>Sludge 1 (S1)</th>
<th>Sludge 2 (S2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage passing the 0.064 mm sieve</td>
<td>66</td>
</tr>
<tr>
<td>Percentage retained over the 0.064 mm sieve</td>
<td>34</td>
</tr>
</tbody>
</table>

Figure 4.78a and Figure 4.78b compare the granulometry of the two sludges.

The second sludge contains gravels with a diameter bigger than 2 mm. The fine inorganic material has the same distribution; indeed both of the two sludges have a similar behaviour during freezing and thawing: the dewaterability (and compaction) is not influenced by the variation of freezing temperature, but is slightly affected by the variation of the number of freezing/thawing cycles.

5.11.2. Treated sludges

Freezing and thawing time

The freezing temperature and the moisture content principally influence the freezing and the thawing time of the two sludges. Figure 4.79a and 4.79b compare the trend of the freezing and thawing time of the sludges placed in the soil tubes.
The first sludge has higher moisture content and, at each freezing temperature, needs more time to freeze than the second sludge. The opposite happens during thawing: the first sludge requires less time to thaw totally. The freezing curves have the same trend, but are staggered few minutes; the same with the thawing curves. This happen probably because the two sludges have the same composition (similar grain size distribution of the fine material), but a different water and oil content.

**Leaching test**

The leaching test is a reliable method to evaluate the compaction of the sludge after freezing thawing and leaching. Figure 4.80 compares the moisture contents obtained with the leaching tests for the first and second sludge. The water losses are bigger for the first sludge because of its higher water content; after 24 hours of leaching, the first sludge reaches a moisture content that is similar to that of the second sludge. To have better results it seems necessary to pre-treat the sludge to obtain a lower initial water content, like in the case of the second sludge: it requires less time to be completely frozen and, after 24 hours of leaching, it has less water content than the first sludge; the choice of starting from a lower or higher water content depends also on the costs for the pre-treatment and the quality of the removed supernatant. It could be interesting to evaluate the water content also after 48 and 96 hours of leaching to have a better knowledge of the water losses.

Figure 4.81 compares the organic matters of the two treated sludges. As already stated, the moisture contents are not influenced by freezing temperatures and number of cycles. The two sludges came from the same workshop, so probably the initial oil content was the same. The second sludge underwent to a deliquoring process, resulting in lower oil content and, consequently, lower volatile solids content.
The plastic limits of the two sludges are different: the treated first sludge has higher plastic limits; that means that it changes its behaviour from plastic to semi-solid before the other sludge; it passes to the semi-solid state with higher water content. The composition of the inorganic material of the two sludges is similar so it is logical to think that the plastic limits should be the same; this difference can be influenced by the different strength in compaction while freezing, depending on the water content, or by the oil content.
The collected sludges analysed in this thesis work came from the same workshop; the initial results showed that the grain size distribution of the two materials was similar, thus a similar behaviour in freezing/thawing was predicted. Water and oil content influence the freezing and thawing time, but while it is well known that a material with elevated water content requires more time to freeze, the effect of the oil has to be clarified. The dewatering, and consequent compaction, of this particular kind of workshop sludge is principally connected with the grain size distribution of the inorganic material. The coarse-grained material is not affected by the freezing conditioning, while the fine-grained material is altered, especially with an elevated number of freezing cycles: formation of voids and increased permeability allow the thawed water to flow away more easily. In any case, the differences between one freezing cycle and three freezing cycles are negligible. This can be due to the presence of oil that bonds together particles, slowing the conditioning of the sludge, but more studies related to the presence of oil in workshop sludges are required. The workshop sludge studied in this thesis work is not affected by the variation of freezing temperature; as shown in the results, the use of different temperatures in the conditioning of sludge does not lead to any changes; that means that it is possible to choose the freezing temperature that is most viable for this kind of treatment. The relation between oil content and dewatering has to be clarified; the freezing conditioning seems not to be able to remove properly the oil from the workshop sludge; in fact, really little oil flowed away from the sieve of the leaching apparatus, for every freezing temperature and freezing cycles; the results showed that the organic content (including oil) has never been affected by the freezing temperature, neither by the number of freezing cycles; this to prove even more that, while the organic matter has been completely trapped over the sieve, just little oil flowed away and there are no visible variations in the organic content of the treated material. The plastic limit was supposed to be a useful instrument to analyse the variation of structure of the fine-grained material in the treated sludge; again, the presence of oil make the results not reliable.

It is possible to draw general conclusions for the two workshop sludges: in order to obtain the best product, it is necessary to use the following freezing parameters:

- the freezing temperature should be set at a value lower or equal to -10°C. Higher temperatures will lead to higher freezing time that can be expensive to maintain;
- one freezing cycle is enough to obtain good results on the workshop sludge. Performing more cycles is not viable;
- the thawing of the material should be performed over a permeable media (like a sieve or a compost bed) in order to let all the liquor to flow away without being retained in the solidified sludge;
- since the freezing treatment doesn’t remove the oil properly, starting with lower oil content will lead of course to better results. This depends principally on the pre-treatment costs and if it is better to perform it before or after the freezing treatment. A summary of what has being said is shown in the following graph.
Chapter 6: Conclusions

- Low oil content

**FREEZING TREATMENT**

**BEST PARAMETERS**
- Freezing temperature below -10°C
- 1 freezing cycle
- Thawing over a permeable media

SLUDGE → FREEZING TREATMENT → BEST PRODUCT
FUTURE STUDIES
Few studies regarding workshop sludges have been done. This essay is just an initial point from where other studies can take cue. The literature review was focused on the studies regarding freezing and thawing of different kind of sludges (especially oily sludges) and soils; no material related to workshop sludge was found. This thesis is just the beginning of a series of studies that can be done; this paragraph will discuss about some possible future studies related to this field that can improve the overall knowledge on workshop sludges and their behaviour while freezing and thawing.

A new test to evaluate the dewaterability of the sludge has been used in this thesis work; in order to evaluate its reliability it is necessary to perform other experiments; first of all some analyses on workshop sludge should be performed in situ, with the FriGeo apparatus, comparing the results with those of the leaching test. This can bring benefits to this new field of studies and advantages to the companies interested in using a freezing apparatus to dewater sludge.

In this essay few freezing parameters have been tested on the conditioning of the sludges. It is possible to improve the general knowledge analysing the effect of the variation of freezing direction on the dewatering of the workshop sludge. Of more interest can be the analysis of the variation of thawing temperature and thawing rate; as an example, it could be interesting to see the effects of thawing a frozen sludge in a water bath or in a microwave.

Since no works have described workshop sludges (especially their behaviour while freezing and thawing at different conditions) another possible future study could be the analysis of a sludge with the same origin of the two already studied, but with different initial characteristics. This essay focused on two sludges, one unaltered and the other one with lower water and oil content; the new sludge should have higher values of these characteristics.

The leaching test is a reliable test that represents what happens while freezing and thawing sludge; it simulates the freezing apparatus used by FriGeo AB to condition workshop sludges, but can be used to evaluate the conditioning of sludges with totally different initial characteristics, collected from different places. An organic sludge derived from a paper factory has been already analysed through the leaching test; the obtained results were satisfactory.

In this essay the leaching test has been used to analyse the material after 24 hours of leaching, but it is possible to analyse the material after 48, 72 and 96 hours, until the material is completely dry; this will allow the drawing of a “water losses” vs. time graph, for each sample, treated with different freezing conditions. An evaluation of the “water losses velocity” is possible as well.

It has been already stated that, in order to be sure of the best and most viable freezing parameters, it is necessary to do a cost analysis. Comparison with other dewatering methods (mechanical or thermo-chemical) should be done as well.
REFERENCES
(IN ALPHABETICAL ORDER)


Jean D. S., Chu C. P. and Lee D. J. (2001b) Freeze/thaw treatment of oily sludge from petroleum refinery plant. Separation science and technology. 36, 2733-2746..............5, 14


References


T. H. W Baker (1991) Personal communication. 6


APPENDIX A
Malningsundersökning

WIN5100 V2.01
Unit 1
S/N 556
Page 1

Sample: SL B3 sample
Operator: LTU
Submitter: LTU
File Name: C:\WIN5100\L7U\06-035.6MP
Material/Liquid: quartz/Water

Test Number: 1
Test Run: 9-11-027 09:12:18
Reported: 9-11-027 09:46:32
Analysis Type: High Speed (Adj)
Run Time: 0:19 hours
Sample Density: 2.650 g/cm³
Liquid Visc: 0.7221 cp
Liquid Density: 0.9941 g/cm³
Analysis Temp: 35.0 °C
Base/Pull Scale: 139 / 115 kOs/s
Full Scale Mass: 100.0%
Reynolds Number: 0.73

Report by Size Table

<table>
<thead>
<tr>
<th>High Diameter (μm)</th>
<th>Low Diameter (μm)</th>
<th>Average Diameter (μm)</th>
<th>Mass Finer (%)</th>
<th>Mass (%)</th>
<th>Frequency (%)</th>
<th>Deviation (Percent)</th>
<th>Cum. Mass (Percent)</th>
<th>1 tests</th>
</tr>
</thead>
<tbody>
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<td>80.00</td>
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<td>0.0</td>
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141
Report by Mass Percent

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<th>Frequency (Percent)</th>
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<td>Mass</td>
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Sample: S1 Wet sample
Operator: 
Submitter: LTU
File Name: C:\WIN5100\LTU\06-035.pmp
Material/Liquid: quartz/Water

Test Number: 1
Analysis Type: High Speed (Adj)

Reported: 9-11-027 09:24:18
Sample Density: 2.650 g/cm³

Liquid Visc: 0.7221 cp
Liquid Density: 0.9941 g/cm³

Analysis Temp: 35.0 °C
Base/Full Scale: 139 / 115 Kcounts/s

Reynolds Number: 0.73

Mass Frequency vs Diameter
Malningsundersökning

WIN5100 V2.01  Unit 1  S/N 556  Page 5

Sample: S1 Wet sample
Operator: 
Submitter: LTU
File Name: C:\WIN5100\LTU\06-035_SMP
Material/Liquid: quartz/Water

Test Number: 1  Analysis Type: High Speed(Adj)
Analysis Date: 9-11-027  09:24:18  Run Time: 0:12 hrs:min
Reported: 9-11-027  09:46:32  Sample Density: 2.650 g/cm³
Liquid Visc: 0.7221 cp  Liquid Density: 0.9941 g/cm³
Analysis Temp: 35.0 °C  Base/Full Scale: 139 / 115 Kcounts/s
Full Scale Mass: 100.0%  Reynolds Number: 0.73

Rosin Rammler Graph

[Graph showing particle diameter distribution]
Malningsundersökning

Sample: Sl Wett sample  
Operator:  
Submitter: LTU  
File Name: C:\WIN5100\LTU06-035.SMP  
Material/Liquid: quartz/Water

Test Number: 1  
Analysis Type: High Speed (Adj)  
Run Time: 0.19 hrs:min  
Reported: 9-11-027 09:24:18  
Sample Density: 2.650 g/cm³  
Liquid Visc: 0.7223 cp  
Liquid Density: 0.9941 g/cm³  
Analysis Temp: 35.0 °C  
Base/Pull Scale: 139 / 115 Kcounts/s  
Full Scale Mass: 100.0%  
Reynolds Number: 0.73

Summary Report

Full scale pump speed: 4  
Stir time: 30 secs  
Bubble detection: Coarse  
Stir speed: Low  
Starting Size: 75.00 μm  
Probe time: 15 secs  
Ending Size: 0.25 μm

Parameter 1 0.000  
Parameter 2 0.000  
Parameter 3 0.000

Mass Distribution Arithmetic Statistics

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<tr>
<th>Number</th>
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<th>Median</th>
<th>Mean Deviation</th>
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<th>Kurtosis</th>
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* Peaks must comprise at least 5.00 % of the distribution.
APPENDIX B

Malingsundersøkning
WIN5100 V2.01
Sample: 82 Dry sample
Operator: 
Submitter: LTU
File Name: C:\WIN5100\LTU\06-036.SMP
Material/Liquid: quartz/Water

Test Number: 1
Analysed: 9-11-027 09:59:49
Reported: 9-11-027 10:12:05
Liquid Visc: 0.7220 cp
Analysis Temp: 35.0 °C
Full Scale Mass: 100.0%

Analysis Type: High Speed(adj)
Run Time: 0:18 hrs:min
Sample Density: 2.650 g/cm³
Liquid Density: 0.9941 g/cm³
Base/Pull Scale: 139 / 125 KOps/s
Reynolds Number: 0.73

Report by Size Table

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### Report by Mass Percent

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APPENDIX B

Malningsundersøkning

WIN5100 V2.01  Unit 1  S/N 556  Page 3

Sample: S2 Dry sample
Operator: 
Submitter: LTU
File Name: C:\WIN5100\LTU\06-036.IMP
Material/Liquid: quartz/Water

Test Number: 1  Analysis Type: High Speed (Adj)
Analysed: 9-11-027 09:59:49  Run Time: 0:12 hrs:min
Reported: 9-11-027 10:12:05  Sample Density: 2.650 g/cm³
Liquid Visc: 0.7220 cp  Liquid Density: 0.9941 g/cm³
Analysis Temp: 35.0 °C  Base/Full Scale: 139 / 126 K Cnt/s
Full Scale Mass: 100.0%  Reynolds Number: 0.73

Cumulative Finer Mass Percent vs. Diameter
Data Sheet:

Sample: S2 Dry sample
Operator: LTU
File Name: C:\WIN5100\LTU\06-036.SMP
Material/Liquid: quartz/Water
Test Number: 1
Analysis Type: High Speed (Adj)
Reported: 9-11-027 10:22:05
Analysis Temp: 35.0 °C
Sample Density: 2.650 g/cm³
Liquid Visc.: 0.7220 cp
Liquid Density: 0.9941 g/cm³
Full Scale Mass: 100.08 kgs
Reynolds Number: 0.73

Graph: Mass Frequency vs Diameter

![Graph Image]
Sample: S2 Dry sample
Operator: 
Submitter: LTU
File Name: C:\WIN5100\LTU\06-036.smp
Material/Liquid: quartz/Water

Test Number: 1
Analysis Type: High Speed (Adj)
Run Time: 0:12 hrs:min
Reported: 9-11-027 08:55:49
Sample Density: 2.650 g/cm³
Analysis Temp: 35.0 °C
Base/Full Scale: 109 / 126 Kcounts/s
Liquid Visc: 0.7220 cp
Liquid Density: 0.9941 g/cm³
Reynolds Number: 0.73

Rosin-Rammler Graph

log log 100/Cumulative Percent Retained

Particle Diameter (μm)
APPENDIX B

Malningsundersökning

WIN5100 V2.01  Unit 1  S/N 556  Page 6

Sample: S2 Dry sample  Operator:  Analyzed: 9-11-027  09:59:49  Analysis Type: High Speed
Operator:  Submitted: LTU  Reported: 9-11-027  10:12:05  Sample Density:  2.650 g/cm³
Submitter: LTU  File Name: C:\WIN5100\L76\06-036.SMP  Liquid Visc:  0.7220 cp  Liquid Density:  0.9941 g/cm³
Material/Liquid: quartz/Water  Analysis Temp:  35.0 °C  Base/Pull Scale:  139 / 126 KCounts/s
Full Scale Mass: 100.0%  Reynolds Number: 0.73

Summary Report

Full scale pump speed: 4  Stir time: 30 secs
Bubbling detection: Coarse  Stir speed: Low
Starting Size: 75.00 μm  Probe time: 15 secs
Ending Size: 6.25 μm

Parameter 1 0.000  Parameter 2 0.000  Parameter 3 0.000

Mass Distribution Arithmetic Statistics

\[ \text{Mode} = 0.251 \quad 0.000 \quad \text{Median} = 15.38 \quad 0.000 \]

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* Peaks must comprise at least 5.00 % of the distribution.