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Briquetting of Manganese Oxide Fines with Organic Binders

How well suited are organic binders for
agglomeration of Mn-oxide fines?

Thomas By

Preface

This project was carried out at the Department of Material Science and Engineering, at the Norwegian University of Science and Technology (NTNU), spring 2017. This was a collaboration project between NTNU and Eramet Norway, through SFI Metalproduction.

I would like to thank my supervisor Leiv Kolbeinsen and co-supervisor Eli Ringdalen for support and wise words throughout my work. I am also grateful for the support from Eramet Norway through Jens Davidsen, Peter Cowx and Per Anders Eidem, it has been of great help.

Abstract

Dust and fines are created throughout the ferromanganese metal production. These fines are collected from ventilation filters, screening operations and off-gas cleaning facilities. As the fines contain a substantial amount of manganese it would be beneficial to charge them to the SAF (submerged arc furnace). Due to furnace design, it is sensitive to fines of sizes smaller than 6mm. These fines clog channels in the charge layer, trapping gas produced deep in the furnace and hazardous situations and unpredictable furnace operation arise.

In this work, manganese containing fines collected and delivered by Eramet Norway has been agglomerated through briquetting in combination with different binders. The binders were; Lime/molasses, magnesium-lignosulfonate and low dosage bentonite, the two first are organic binders and bentonite inorganic. The organic binders were tested in different dosages and were the focus area of this thesis.

Two briquetting techniques were performed; uniaxial pressing and roll pressing. The uniaxial pressing was used to compare binders directly in green state (made but untreated), where it was concluded that the highest dosages of lime/molasses and lignosulfonate gave the strongest green strength briquettes.

The two high-dosage organic binder briquettes were then reproduced with the roll press technique, which is the production method which is considered for industry purposes, to investigate further furnace operation potential. They were strength tested in green state and treated at different temperatures; 105°C, 300°C, 500°C and 800°C prior to compression strength testing. The evolution of strength from heat treatment gave the results of strength gain when dried, then steady decrease in strength from 300°C up to 800°C, this most probably due to organic binder burn-off at around 300°C. This leaves the briquettes weakened for a long temperature interval and strength gain from sintering is not believed to occur before 1200°C is reached.

From long-term storage, it was noted that none of the different binder briquette types decreased notably in strength from storage intervals of 5 weeks. It is believed that mold formation in stored briquettes will not be a problem if stored for less than 30 days in a humid environment, or if stored dry, longer storage times will be possible.

Sammendrag

Finstøv oppstår hele veien i ferromangan-metallproduksjonen. Finstøv blir samlet opp fra ventilasjonsfiltre, sikting av knust malm/metall og fra renseanlegg for avgass. Ettersom finstøvet inneholder en betydelig mengde mangan, vil det være fordelaktig å mate dem til SAF-ovnen (nedsenket lysbueovn) for gjenvinning. På grunn av ovnsdesign er den følsom for støv av størrelsesorden mindre enn 6 mm. Dette finstøvet tetter kanaler i råmateriallaget og fangst av gass produsert dypt i ovnen og farlige situasjoner oppstår og gir uforutsigbar ovndrift.

I dette arbeidet har manganholdig finstøv, samlet og levert av Eramet Norge, blitt agglomerert gjennom brikettering i kombinasjon med forskjellige bindemidler. Bindemidlene var; kalk/melasse, magnesium-lignosulfonat og lavdose bentonitt, de to første er organiske bindemidler og bentonitt er uorganisk. De organiske bindemidlene ble testet i forskjellige doseringer og var fokusområdet for denne oppgaven.

To briketteringsteknikker ble brukt; en-aksiell pressing og rullepressing. Resultatene fra den en-aksielle pressen ble brukt til å sammenligne bindemidler direkte i grønn tilstand (laget, men ubehandlet), hvor det ble konkludert med at den høyeste dosen kalk/melasse og lignosulfonat ga de sterkeste grønne brikettene.

De to høydoserede organiske bindemiddelbrikettene ble deretter reprodusert med rullepresseteknikken, som er produksjonsmetoden som anses å bli brukt for industrielle formål, for å undersøke ytterligere ovnsoperasjonspotensial. De ble styrketestet i grønn tilstand og behandlet ved forskjellige temperaturer; 105°C, 300°C, 500°C og 800°C før testing av kompresjonsstyrke. Utviklingen av styrke fra varmebehandling ga styrkeøking når de ble tørket og deretter jevn reduksjon i styrke fra 300°C til 800°C, dette skyldes trolig at disse organiske bindemiddel brenner av ved 300°C. Dette etterlater brikettene en svekket tilstand i et langt temperaturintervall, og styrkeforsterking fra sintring antas ikke å forekomme før 1200°C er nådd.

Fra langtidslagring ble det bemerket at ingen av de forskjellige bindemiddelbrikett-typene hadde en tydelig reduksjon i styrke etter 5 ukers lagringstid. Det antas at muggdannelse i lagrede briketter ikke vil være et problem om lagringstiden blir holdt kortere enn 30 dager i et fuktig miljø, og hvis de oppbevares tørt, vil det være mulig med lengre lagringstid.

Sammendrag

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1. Introduction

Ferromanganese production is important for the steel industry, where manganese is a crucial alloying element. One problem in the ferromanganese industry is that dust containing substantial amounts of manganese is generated throughout the metal production process. It arises from the crushing and screening of both raw material ore and finished alloy, it is collected in filters over and around the furnace and refining modules and from off-gas cleaning and mercury separating facilities. For the industry, utilization of this dust will represent an increased amount of metal produced from the raw materials purchased, thus a better economic gain from the production.

The main problem with these manganese rich fines (dust) is that it is extremely hazardous to charge it directly to the furnace in combination with the normal sized ore and other raw materials. These fines will clog the channels the gas produced deep in the furnace use to ascend out through the top of the furnace, leading to bad furnace operation and an increase in the possibility of explosion.

Agglomerating such fines is a method used in the iron production that gives the possibility to use waste fines anew and yields satisfactory results. Agglomeration is the process of bonding small particles into larger components and has proven itself useful in iron production through pelletizing.

Agglomeration often makes use of a binder to collect and bond fines, and up until recently, the binders have mostly been inorganic cementous and clay materials, but these introduce unwanted elements to the smelting operation. Due to this, organic binders are in the wind as a substitute for the traditional inorganic binders, as these organic compounds introduce little to no impurity elements to the smelting process.

In this work, briquetting has been the selected agglomeration method. Briquetting make use of pressure in combination with a binder to densify and bond particles. Two different organic binders and one inorganic binder has been utilized and the finished agglomerates (briquettes) were tested for their strength.

From a project work done in the fall of 2016 at NTNU, it was observed that organic binder briquettes stored for longer periods started to self-disintegrate and heavy mold growth was observed.

The goal with this work is to investigate the potential of organic binders in briquetting of manganese oxide fines for ferromanganese alloy production. This will be tested in terms of compression strength, fines produced from rough treatment, effect of temperature on strength and how they tolerate storage.

2. Background

2.1. Production of Ferromanganese Alloys

The ferromanganese production takes place in an electric SAF (submerged arc furnace) as is depicted in **Figure 1**. The general production reaction is a thermal reduction with a reducing agent. Raw material is fed into the furnace where it reacts with carbon from the coal bed, electrodes and CO gas used to heat the charge.
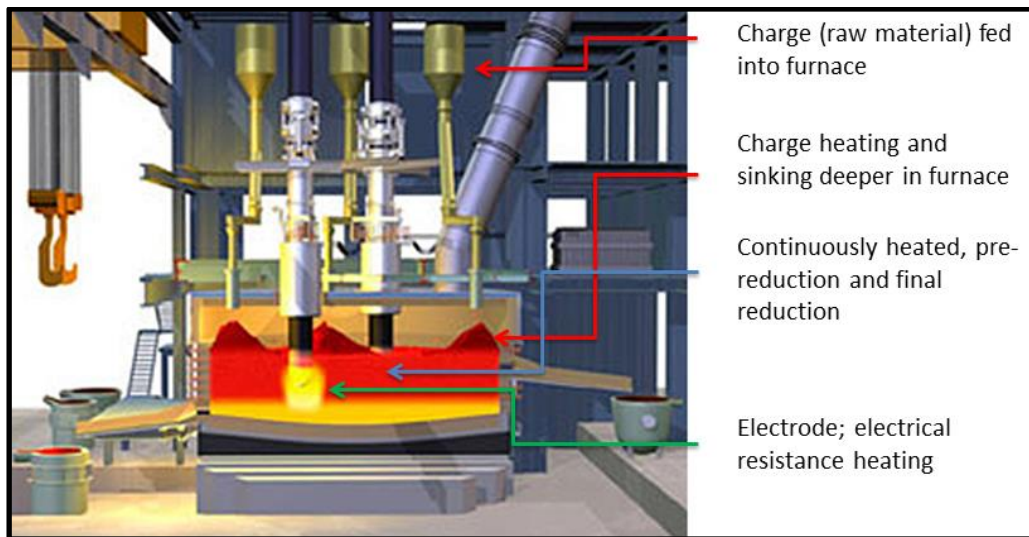
Figure 1: Illustration of an electric submerged arc furnace [1]

2.1.1. Main Furnace Reactions

The main process of manganese production follows these reduction reactions:

$$MnO_2 + \tfrac{1}{2}CO = \tfrac{1}{2}Mn_2O_3 + \tfrac{1}{2}CO_2 \qquad \Delta H°_{298} = -99.9kJ \qquad (1)$$

$$\tfrac{1}{2}Mn_2O_3 + \tfrac{1}{6}CO = \tfrac{1}{3}Mn_3O_4 + \tfrac{1}{6}CO_2 \qquad \Delta H°_{298} = -31.3kJ \qquad (2)$$

$$\tfrac{1}{3}Mn_3O_4 + \tfrac{1}{3}CO = MnO + \tfrac{1}{3}CO_2 \qquad \Delta H°_{298} = -16.9kJ \qquad (3)$$

$$\tfrac{1}{3}C(s) + \tfrac{1}{3}CO_2(g) = \tfrac{2}{3}CO(g) \qquad \Delta H°_{298} = 57.5\ kJ \qquad (4)$$

$$\tfrac{1}{3}Mn_3O_4(s) + \tfrac{1}{3}C(s) = MnO(s) + \tfrac{1}{3}CO(g) \qquad \Delta H°_{298} = 40.6\ kJ \qquad (5)$$

$$MnO(l) + C = Mn(l) + CO \qquad \Delta H°_{298} = 252.3kJ \qquad (6)$$
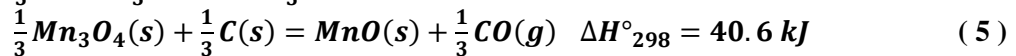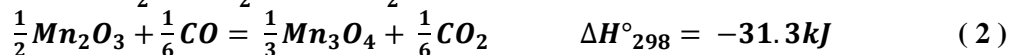
Depending on the ore used, the amount of the different valence state manganese oxides differs. **Equations (1)-(3)** are exothermic with $\Delta H°_{298}$of -99.9kJ, -31.3kJ and -16.9kJ, respectively [2]. This will produce additional heat as the reactions proceed, contributing to pre-heating of the charge. The reduction-rate of these equations are slow at low temperatures. Taking for instance MnO_2 to Mn_2O_3, equilibrium calculations imply that the reaction should proceed easily at room temperature, but the reaction only starts to proceed at noticeable rate from 400°C, leaving kinetics as the main hindrance[2]. As the temperature rises above 800°C, reduction at the surface of the coke is sufficiently rapid to reduce Mn_3O_4. At these temperatures, the Boudouard reaction **Equation (4)**, will run simultaneously to the reduction of Mn_3O_4. Combining **Equations (3)** and **(4)** leads to the total reaction of **Equation (5)**.

Equation (5) is called a direct reaction with carbon, although it takes place through a gas phase. Since the Boudouard reaction is strongly endothermic ($\Delta H°_{298} = 57.5 kJ$), the overall reaction will be endothermic as well.

The final metal producing reduction, **Equation (6)**, is an endothermic reaction with enthalpy of $\Delta H°_{298} = 252.3 kJ$. In addition to pure Mn(l), carbon will be dissolved in the metal up to saturation.

Iron oxides are constantly present in the manganese ore, iron reduction will run alongside the manganese reduction. For iron, reduction from FeO to Fe is possible through direct reduction, which is not possible for MnO, as MnO is far more stable than FeO.

2.1.2. Raw Materials

Ore

Manganese oxides are found with manganese in its divalent, trivalent and tetravalent state in the ores used for manganese production. The different valence-state oxides differ in behavior for furnace operation due to the difference in reduction path, as shown in the previous section through **Equations (1)-(6)**. The manganese ores are mainly classified in three categories[3]:

Metallurgical ores – Mn-content between 35wt% to 50wt%
Ferruginous ores – Mn-content of 15-35wt%
Manganiferous ores – Mn-content of 5-10wt%

Metallurgical ores are used for production of high carbon ferromanganese and silicomanganese alloys due to the high manganese content. Another important parameter is the amount of iron in the ore. A weight ratio [Mn/Fe] of 7.5 is required for producing a 78wt% Mn ferromanganese alloy. The content of alumina and silica should be limited, as it will increase the slag formation and further increase the electricity consumption for the production. The phosphorus content is a key parameter as well and metallurgical ores with phosphor content less than 0.1wt% may earn the right of a premium mark[3].

The ferruginous and manganiferrous ores are used in blast furnace iron production to adjust the Mn content of produced pig iron.

Fines from the excavation of Mn ores are agglomerated and sintered. These products are suited for use in the ferromanganese furnace due to its mechanical strength and thermal stability, leading to an even distribution of gas used in the pre-heating and pre-reduction zones. This is important to ensure evaporation of water before it reaches the smelt, as that may lead to unwanted furnace behavior and in worst case explosion[4].

Carbon Material

Coke

Coking is a refining process of coal, where coal is heated under absence of air to evaporate volatile formations embedded in the coal. The coking is divided in low temperature and high temperature coking, where high temperature coking is carried out at temperatures above 1000°C. This coke is what is used for the FeMn production today[3].

To prepare for coking, the coal is crushed to a size where 80-90% passes through a 3mm sieve. Several types of coals are blended in this step. Almost all metallurgical coke is produced in coke-oven batteries consisting of up to 80 ovens. The width of the oven is normally 0.4-0.6m, the length 10-20m and a height of 6-8m. The coal charge is heated by conduction for 14-20 hours. Temperature range from 350-500°C during heating, the coal passes through a partly fluid state and above this temperature the fluid solidifies to solid coke. Almost all volatiles are expelled during this step, leading to a final volatile concentration of about 1-2wt%[3].

The chemical properties of the coke control the reactivity, amount of reduction, total material used and as well the energy consumption of the smelting process. The physical properties however, will only affect the efficiency and productivity of the furnace to some extent[3].
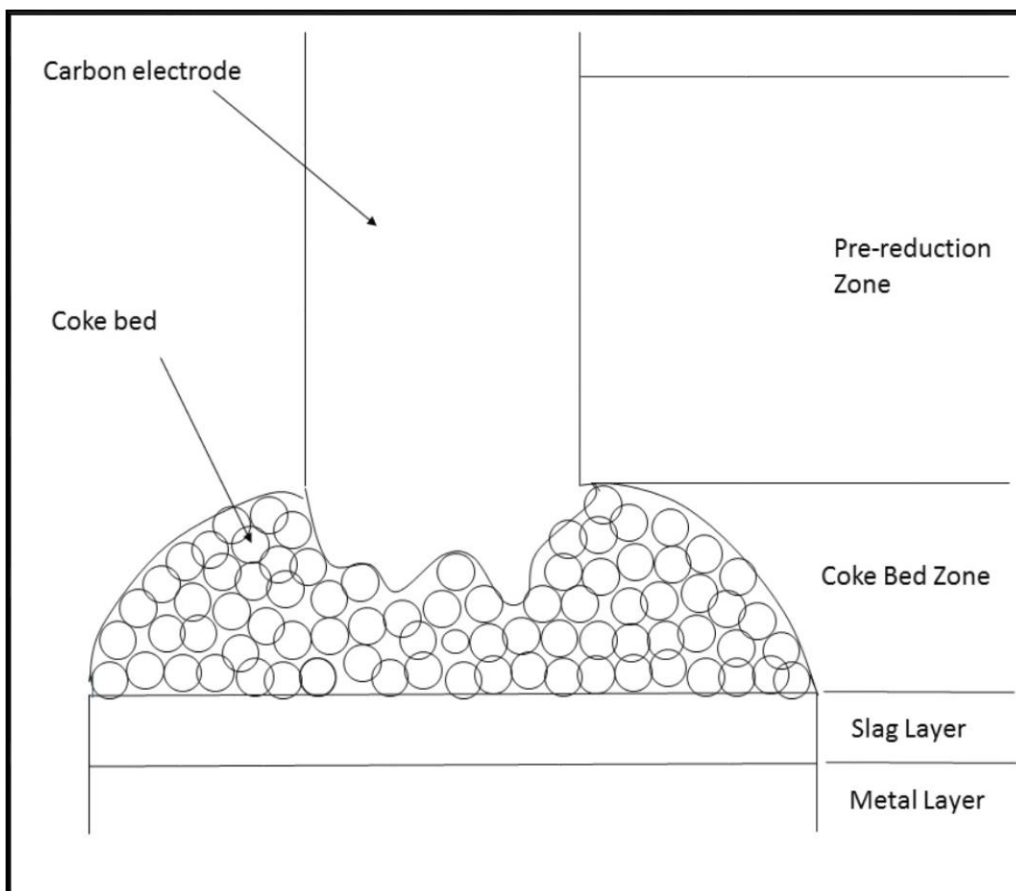
2.1.3. Physical Furnace Zones

Figure 2: Different zones inside the SAF; pre-reduction, coke bed, liquid slag layer and liquid metal layer

<u>Background</u>

The furnace can be characterized with four main zones. The top layer, which contains solid raw material, is classified as the pre-reduction zone. Further down in the furnace is the coke bed on top of the slag and around the bottom of the electrodes, which is where the metal producing reaction takes place. Under the coke bed is the slag layer, then at the bottom is the metal layer (see **Figure 2**).

2.1.3.1. Pre-reduction Zone

Manganese ore consists of different valent Mn-atoms. While heating up to 1000°C, the high valent Mn-oxides will undergo reduction by CO gas. These reduction steps, *Equations (1)-(3),* are all exothermic reactions and MnO will be the final product of reduction by gas.

The CO gas is produced in the coke bed zone and ascends in the SAF, up through the charge where it reacts with the ore material. Since the gas is hot, it will heat the charge on the way out of the furnace, so that the charge achieves a gradually increase in temperature as it descends to reaction zone/coke bed zone. Because the pre-reduction is exothermic, these reactions will contribute to the heating of the charge as well. **Figure 3** gives an indication of which temperature ranges the different reductions occur. In addition, with the rising temperature, the charge will be dried at the top of the SAF. This hinders water from entering deep down in the SAF, assuring no water contained within the smelting zone. If water is trapped deep in the furnace, explosion by evaporation of water occur[2].
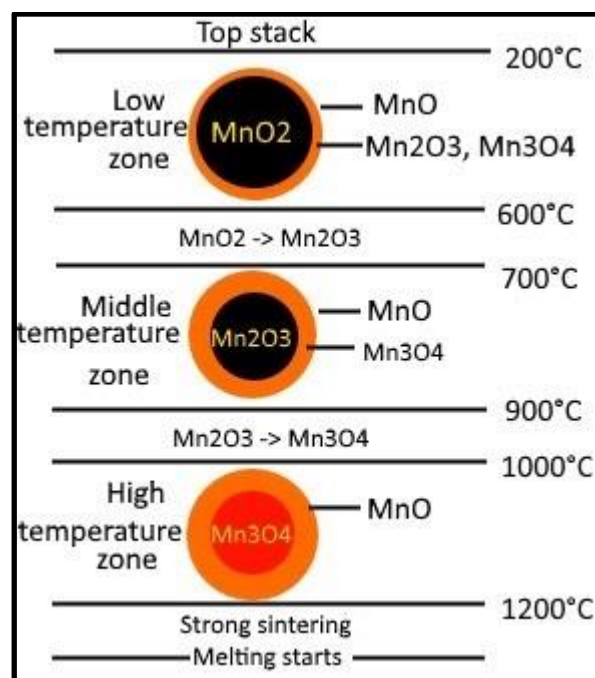
Figure 3: Suggested reaction progress for a MnO2 lump [5]

The final metal producing reaction, *Equation 6,* produce CO-gas as a byproduct. This gas is produced far down in the furnace and has to proceed out of the top, or else the partial pressure of CO will build up and may lead to explosion as well[6]. This unwanted situation may occur if the top layer of the furnace is too densely packed. It is therefore important for the charge

fed to the furnace to have sufficient number of channels, for the gas to flow out through the top of the furnace and into the ventilation system. This is achieved by good size control of the charge materials.

2.1.3.2. Coke Bed Zone

The metal producing reaction (*Equation 6*) takes place in the coke bed zone. After complete pre-reduction, 90% of the composition will be of MnO, SiO_2 and Al_2O_3, where MnO will amount to about 80%. As the oxides melts down, coke particles will settle on top of the permanent coke bed. The coke bed zone starts approximately at the tip of the electrodes, and the relative amount of carbon in the charge determines the size of the coke bed[7].

The coke bed contains the chemical reducing agent for the reduction while it works as a heating element for the process. Through electrical resistance, the coke is heated and energy is transferred to the surroundings. The electrical characteristics of the coke are of importance for the heat distribution and energy of the system, which will determine the production rate, quality and stability of the operation.

When the temperature increase from 1200°C, the ore will sinter, soften and melt. Sintering starts at about 1200°C, softening at about 1300°C. As it melts, there will be a solid phase of MnO in coexistence with liquid slag and the liquid phase will mainly consist of MnO, Al_2O_3 and SiO_2. Above this temperature, the slag is sufficiently viscous to enter the coke bed, and will contain some solid MnO-particles. High surface tension between coke and slag leads to low wetting angle, making the melted ore particles gather and coalesce [7].

At low temperatures, this slag will remain on top of the coke due to high viscosity. As the temperature increase further, the slag will run through the coke bed and the contact area increases, leading to an increase in reduction rate of MnO. The main reduction takes place in the two-phase region liq. + MnO.

2.1.3.3. Slag Zone

Slag from the FeMn-production mainly consists of MnO, CaO, MgO, SiO_2 and Al_2O_3. To describe equilibrium, melting properties and final composition of the slag, the basicity ratio is introduced (*Equation (7)*). This slag basicity ratio is the mass ratio of basic to acidic slag components. CaO and MgO are basic, while Al_2O_3 and SiO_2 are acidic oxides.

$$B = \frac{CaO + MgO}{SiO_2 + Al_2O_3} \qquad (7)$$

Using the three-phase diagram MnO-Al_2O_3/SiO_2-CaO/MgO, the B-value can be used to draw the reduction path of MnO, if only MnO is significantly reduced. Tapped slag from a process with B = 0.65 will typically have a composition of 39% MnO, 26% SiO_2, 11% Al_2O_3, 21% CaO and 3% MgO, which often is the composition of industrial slag tapped at 1400°C[8].

2.1.3.4. Liquid Metal Zone

The metal produced in this process is forming a liquid layer at the bottom of the SAF. The slag and metal is kept separate by difference in density, leading to the less dense slag being on top of the liquid metal. The electrical current running between the electrodes will mainly run through either the metal phase or the coke bed, depending on the electrode tip position. If the electrode tip is placed deep in the furnace, most of the current will go through the metal and with higher position the current will mainly run through the coke bed.

Liquid metal will be extracted through a tapping procedure. The liquid slag will be flowing out after the metal is extracted. Some furnaces operate with tap holes in different heights, where the top hole is for tapping of slag and the bottom for metal[2].

2.2. Agglomeration

As preparation of ore creates a lot of small fines, much raw material may end up unused. To exploit more of these fines, agglomeration is a possible solution. Agglomeration is the process of particle size enlargement and most commonly refers to the upgrading of material fines to larger particles. The most common ones of these are pellets and granules. All types of agglomeration fall in under one of two main categories; pressure agglomeration or non-pressure agglomeration[9].

2.2.1. Pressure Agglomeration

Pressure agglomeration uses compression force to shape a material into the desired form. In this technique, little to no moisture is normally needed, as the pressure will contribute to cohesion between the particles being agglomerated[9].

Most common types of pressure agglomeration-products are briquettes and granules. Briquettes are made with either pillow-shaped forms or with a hydraulic press with a piston and a die, and granules are made by compacting fines into a sheet form, then breaking them up into smaller pieces. Both are normally considered a dry process.

2.2.2. Non-pressure Agglomeration

Non-pressure agglomeration uses a tumbling process to grow fines particles into spherical pellets. A binder, or just moisture is used to assist in acquiring the desired shape. Because of the high moisture content in pelletizing processes, it is considered a wet process[9].

The tumbling is divided in two categories; disc-, and drum pelletizing. In the disc pelletizing, feedstock material and binder are continuously fed on to the disc, where pellets tumble and pick up more fines as they roll, in the same way a snow ball pick up more snow as it rolls down a hill. The drum operation makes use of the same tumble and growth as the disc, but on a larger scale. Drums are often preferred to disc due to their high throughput and the acceptance of large variance of feedstock material.

2.3. Binder Materials

Combining fines with an adhering material, binder, to help hold the shape of the agglomerate is a solution to help with making cold bonded agglomerates. Binder materials are widely used in concretes and are divided in two groups: hydration-hardening binders and chemical binders. The first group includes binders based on systems consisting of an alkali/alkali-earth oxide and a refractory oxide (alumina-, magnesia-cements) [10]. Chemical binders include molecular or colloidal dispersed solutions and inorganic sols, characterized by their polymerization behavior of hardening. Some types of the last mentioned are liquid glass, phosphate binders and oxychloride solution silica [10].

3. Theory

3.1. Collected Fines

Fines and dust are collected at different filters at a ferromanganese production plant. **Figure 4** shows an outline of the cleaning facilities at Eramet Norway, Sauda. From the filter above the refining unit, MOR-dust is collected, while the filters above the furnace and tapping collects environmental dust and cooler dust. From the off-gas cleaning, other fines are captured and flushed out with the process water. These are thickened as water is drawn out and set aside as sludges. In addition to the fines collected by filters and cleaning facilities displayed in **Figure 4**, a lot of fines are created during crushing of the manganese ore and finished alloy. These fines are screened out and set aside as they are too small for use in the charge material or to be sold as alloying element for the steel industry. The crushed ore and metal have a high Mn-content, which still could be valuable.

At INFACON XI a safety limit for amounts of fines fed to both a closed and open SAF was proposed. The recommended limit was set to 15% for the closed furnace and 25% for an open furnace[11].
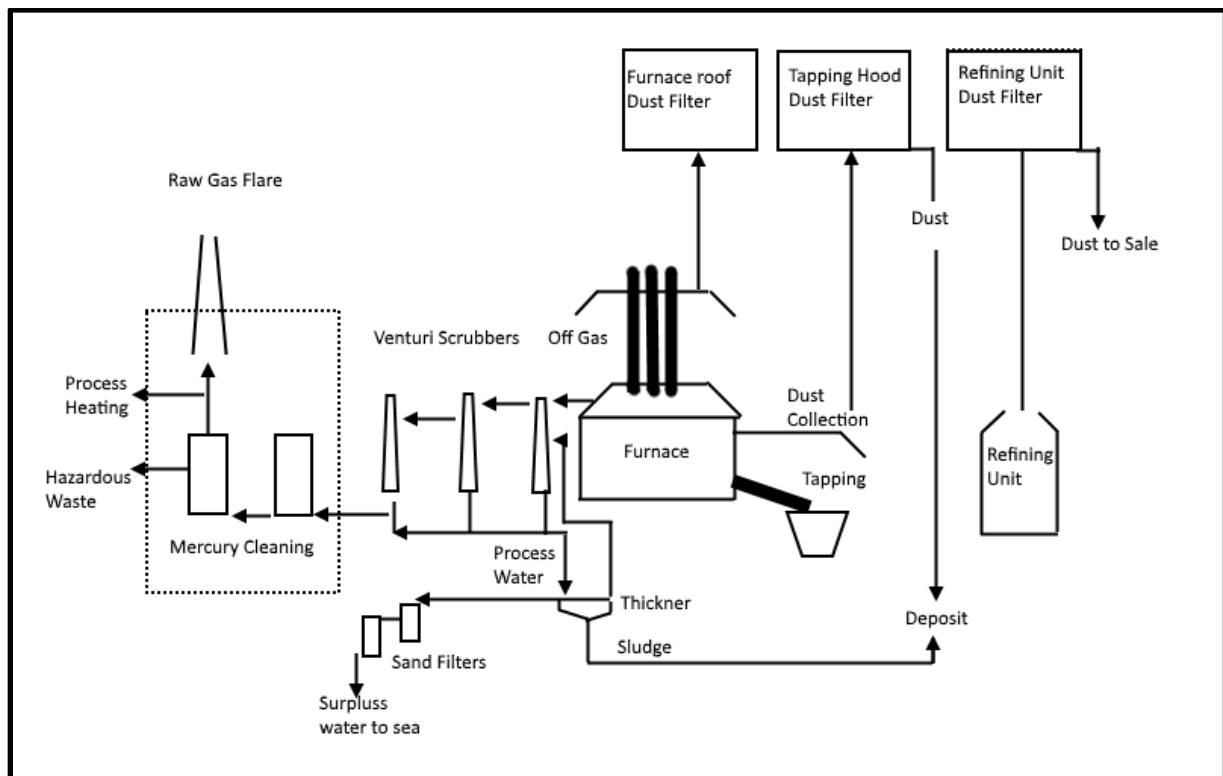

Figure 4: Schematic diagram of the cleaning facilities at Eramet Norway, Sauda. Dust is collected in many different filter systems around the plant [12].

3.2. Briquette Properties

As mentioned, briquetting is a technique of agglomeration which uses pressure to acquire larger shapes from smaller dust particles. When characterizing these briquettes, there are some important terms; green strength, dry strength and burnt strength.

Green strength denotes the strength of briquettes who have not been through any temperature treatment. In the green state (made, but untreated), the briquettes undergo rough handling during transport to and on conveyor belts. Briquettes will experience drops during transport as well. Due to this handling, green strength is an important characteristic. They may also be stored for some time, leading to the ability to withstand compression forces being an important criterion.

When in green state, agglomerates rely on the interparticle bonds to keep its strength. In agglomeration with use of binder, this bond strength is given by the strength of adsorption to the particles and the binder bridge between the particles [13].

Dry strength is the strength of briquettes after surface and loosely bonded water is evaporated from the green briquette. As water is one of the ingredients providing forces to keep the shape of the briquettes, drying leaves the binder with the task of keeping the briquette intact alone. If the binder is not evenly distributed, a lot of dust will be released after water has been evaporated.

For most binders, the strength increase when going from wet/green agglomerates to dry. The bridging created by the binder cure and strengthen, creating a stronger, more robust agglomerate. This phenomenon has been shown to hold for most binders and for different types of agglomerated particles [14] [15]. When dry state of the briquettes is achieved during the manganese production, most of the transport is finished and they have reached the top of the furnace. From this stage, they will be exposed to compression and abrasive grinding in the charge.

Burnt strength is the strength of briquettes as they are heated. While descending in the SAF together with other charge material, the briquettes will gradually be heated. In this phase of operation, they must avoid disintegrating while being exposed to increasing pressure and abrasive wear. The binder is then needed to avoid this until such a temperature is reached so that sintering starts and become the main mechanism of bonding.

The general strength of an agglomerate in all stages is highly dependent on the density, or number of pores. As the number of pores increase, contact points between particles are lost and the strength will decrease [16].

3.3. Binder Mechanisms

Binder materials works by covering multiple surfaces in a continuous medium, connecting them to each other through the binder. To ensure a best possible connection, it is important for the binder to completely cover the surface, e.g. having a small wetting angle. This ensures good contact between binder and particles, further creating strong agglomerates. The strength of the bond between a liquid binder and a solid surface is described by the parameter; work of adhesion (W_A). This parameter should be as large as possible, and is a measure of surface free energies of surface interfaces between solid-vapor, solid-liquid and liquid-vapor, γ_{SV}, γ_{SL} and γ_{LV} respectively[17]. W_A is described by **_Equation 8_** underneath, and

<u>Theory</u>

Figure 5 shows the connection of the surface energies and the wetting angel θ. Combining ***Equations (8)*** and ***(9)*** will give the Young-Dupré equation, which denotes W_A in terms of θ (***Equation (10)***).

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \qquad (8)$$

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} * \cos(\theta) \qquad (9)$$

$$W_A = \gamma_{LV}(1 + \cos(\theta)) \qquad (10)$$
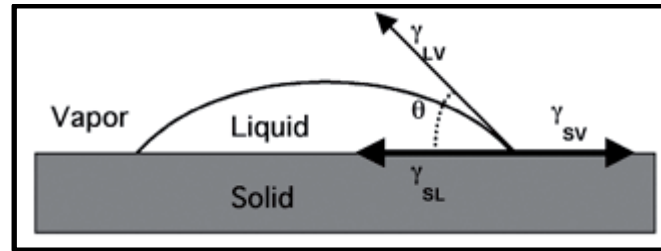
Figure 5: Relationship between surface free energies of the interfaces solid-liquid (γ_{SL}), solid-vapor (γ_{SV}) and liquid-vapor (γ_{LV}). θ is the wetting angle of liquid on a solid surface [17].

From the iron/steel production industry, the inorganic binder bentonite is the one used to the largest extent in pelletization of iron ore concentrates, as it provides good physical quality at all stages of agglomeration. However, since bentonite is a clay material consisting of layers of Al-Si containing oxides, it is sought after to find a replacement, as aluminum and silicon creates acidic oxides and are unwanted impurities. This has led to the search for other binder materials [18]. Organic binders are currently the most promising substitute, as they add low to no amount of unwanted impurities to the smelting process. The largest problem in using an organic binder is that they burn off at relatively low temperatures, leaving the agglomerate with low strength in intermediate temperatures, before sintering takes place.

The way a powder is nucleated by a wet binder is illustrated in **Figure 6**. First, the drop will fall on top of the powder bed, then penetrate lower into the bed pores, vetting the particles of the powder. Capillary forces are the main driving forces for penetration of liquid binder into the powder bed[13]. A study performed on viscosity dependence on nucleation rate of granules found that an increase in binder viscosity will have a retarding effect on nucleation[19]. For agglomerates to have a small spread in physical properties, the binder should be evenly distributed between the particles. If the binder is evenly distributed, all particles should have the same properties [20].

<u>Theory</u>

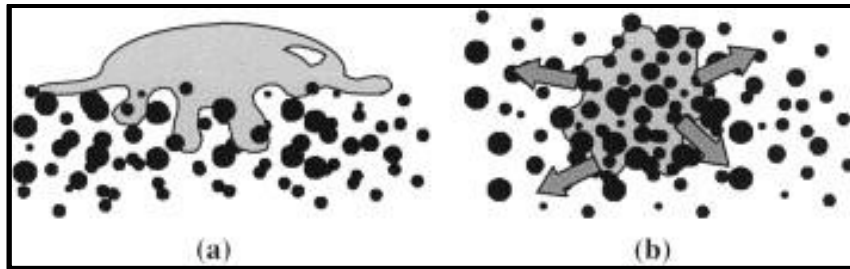**Figure 6: Single drop nucleation. (a) initial nuclei formation due to imbibition of the drop into the powder. (b) Liquid migration within the powder bed causing nuclei growth [13].**

In a study conducted by Kenningley et al. [21], a relationship for breakage or survival of binder-made granules was developed. This relationship states that the amount of impact deformation and breakage in an agglomerate will increase with increasing size of the agglomerate and decreasing viscosity of the binder.

3.3.1. Inorganic Binder

As mentioned, bentonite is an inorganic binder. Bentonite is a clay material which uses a network of layered hydrate aluminosilicate, with montmorillonite as main compound, which has the chemical formula; $(Na, Ca)_{0.33}(Al_{1.67}, Mg_{0.33})Si_4O_{10}(OH)_2 \times nH_2O$ [22]. This structure has a net negative charge which is balanced by surface adsorption of cations. Dry strength in ilmenite pellets for iron and steel production is increased by water evaporating from between the bentonite layers, which decrease the interparticle distance. As the interparticle distance decrease, an increase in van der Waals forces is obtained. At the same time, the clay creates a bridge structure of hardened gel connecting particles[22].

3.3.2. Organic Binder

Organic binders consist of long carbon chains containing functional groups at the chain ends which bonds to the surface of the particles to be agglomerated. These chains create a bridging structure connecting particles after the solvent is dried off. In addition to the bridging effect; Van der Waal's forces are interacting between the chains ensuring stronger connected agglomerates [23].

One organic material that has found many uses the last decades is lignosulfonate (LS), because of its stabilizing, adhesive and complexing properties. LS is obtained as an unwanted by-product from the sulfide pulping of softwood [24] and its most basic structure is shown in **Figure 7** below. From this process, LS is produced in a large spread of molar mass. LS are crosslinked polydisperse polyelectrolytes where the molecules are compact spheres in aqueous solutions [25]. The molecule contains sulfate, carboxylic, phenolic and methoxyl groups. As a binder material, high molar mass (long chained) LS is used [26]. Research performed by [27] on LS binders in cementitious materials states that the higher molar mass fraction of LS is the one that creates bonds to the surface of particles, further creating the bridging structure between them. One drawback from the use of LS as an agglomerate binder for melting furnace operations is that this will add sulfur to the process[18].

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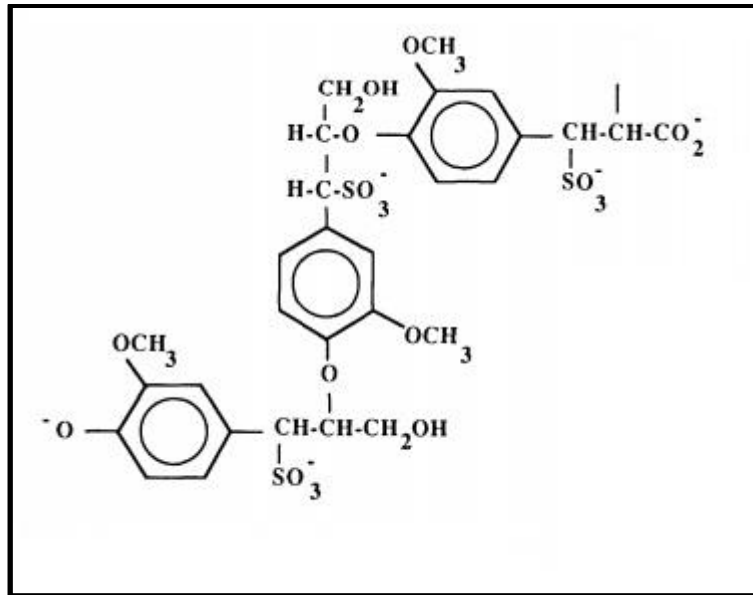
Figure 7: Basic structure of lignosulfonate ionic molecule.
The basic repeating building unit is a phenylpropane
derivative. Bonding is obtained by interactions between
SO₃-groups and the particle surface [28].

Molasses is a binder that has been given more attention lately. Molasses is a byproduct from sugar refining and is a highly viscous liquid [29]. Molasses alone is not considered a strong binder, but in combination with certain materials, such as Ca^{2+} (often added as hydrated lime $(Ca(OH)_2)$), it yields better results [30]. Hydrated lime is added and mixed with the molasses, where the lime first reacts with sucrose sugar from molasses to form a calcium-sucrose complex, then further reacts with CO_2 from the air to form a binding calcium carbonate network. The molasses essentially acts as a catalyst to produce this calcium carbonate network [18].

A study of briquetting of zinc oxide fines [31] found that hydrated lime in combination with dextrin (a low molecular weight carbohydrate) yielded better results in briquette strength during compression and weathering resistance, than in combination with molasses. The same results were also found by Sah and Dutta [32], where the lime and molasses marginally yielded too weak results for use in iron ore pellets, while with the dextrin instead of molasses, the strength was above the set boundary.

3.3.2.1. Burn-Off of Binder

Organic binders will decompose at elevated temperatures. They react with the atmosphere and leave the ceramic material in a gas phase. High temperature and fast decomposition of organic binder may lead to internal cracking in a pressed ceramic material, as the voids left after the binder will not be completely filled as the binder is decomposed. Organic binders may as well leave behind a carbon residue, this if fired in a reducing atmosphere or if the temperature is raised too rapidly, causing uncomplete decompensation [33]. Studies performed on iron oxide pellets suggests that the burn-off temperature is around 300°C for a variety of organic binders[14].

3.3.2.2. Mold Formation

From a pre-study for this thesis work, there was found excessive mold growth on the organic binder briquettes [34]. This was most prominent in the lime and molasses binder briquettes and the mold had a green/blue color. For mold to grow, there are certain conditions that must be met. The fungi need a surface with access to nutrition and loosely bonded water. Humid air is also beneficial for the growth and the air in contact with the surface should hold an average of over 85% humidity for at least a period of 30 days for visible mold growth to occur [35].

3.3.3. Sintering

Sintering is a mechanism of strengthening and compacting of agglomerates. Sintering is a removal of pores between particles, combined with growth together and strong bonding between adjacent particles [36]. For sintering to be possible, a mechanism of transport must be present and an energy sufficient to activate transport must be in place. Heat is the primary energy source for sintering and the sintering procedure is often divided in three stages.

The first stage, or initial stage, is rearrangement of particles and neck formation, where particles rotate slightly to create more contact points between them[36].

The second stage, intermediate, is where the necks between particles grows. This reduces porosity as the centers of the original particles move closer together and shrinkage in the material is equal to the porosity decrease. The contact points are now grain boundaries, and the larger grains increase in size, while the smaller decrease. The second stage proceeds until pores are isolated[36].

The third and final stage of sintering is when the final removal of porosity occur. The isolated pores are removed by vacancy diffusion along the grain boundaries, which leaves a dense and compact final product[36].

Sintering is one technique used for handling and agglomeration of manganese ore fines. Manganese ore fines sinter reach temperatures of 1300°C for a short time, about 1 min, then goes down to approximately 850°C when finished[37]. From the ROMA-project (Norwegian collaboration project between industry and NTNU) it was found that the charge material will not start to agglomerate by sintering until a temperature of 1200°C has been reached[38].

3.3.4. Size Distribution

Agglomeration is very sensitive to the size distribution of particles. Particles of size 1-3 mm act as a nucleation site, while particles smaller than 0.2 mm act as an adhesive layer. Particles in the size range of 0.2-1 mm should be kept to a minimum, as these neither act as a nucleus nor an adhesive layer [39].

3.4. Mixing of Coarse Grained Materials

Coarse grained mixes consist of particles with a large spread in particle sizes, all from larger, very coarse particles to small fines. These particles tend to segregate, creating local density variations within the particle mix. Proper mixing is to obtain uniformity that is retained during handling and die filling [40].

Gravity is a factor contributing to segregation of such a mix. If a mix consists mainly of coarse particles, fines tend to sift to the bottom, making the bottom of the mix more densely packed. In a mix where coarse particles and fines make up approximately the same volume, the segregation effect of gravity is much smaller. If the volume of the mix is filled mainly with fines, the coarse particles will tend to segregate to the bottom, and the mix will be nonuniform [40].

Shear segregation is another mechanism that separates the coarse and fine particles. In a fluid shear field, coarse particles are situated in the high velocity zones.

When mixing with a binder present, the binders task is to keep the fine particles adhered to the surface of the coarse particles, as means to avoid segregation.

There are many types of equipment on the marked for mixing dry powder, such as; high intensity mixers, mullers, sigma blade mixers, V blenders and ribbon blenders. The most known high intensity mixer is perhaps the Eirich type, and the most common among those is the one with high-speed, vertical shaft impeller and plow blade (see **Figure 8**). The impeller is placed out to the side of the center within the rotating pan, and is rotating in the opposite direction of the pan itself. The stationary plow blade is situated behind the impeller and is helping to distribute the mix [40].
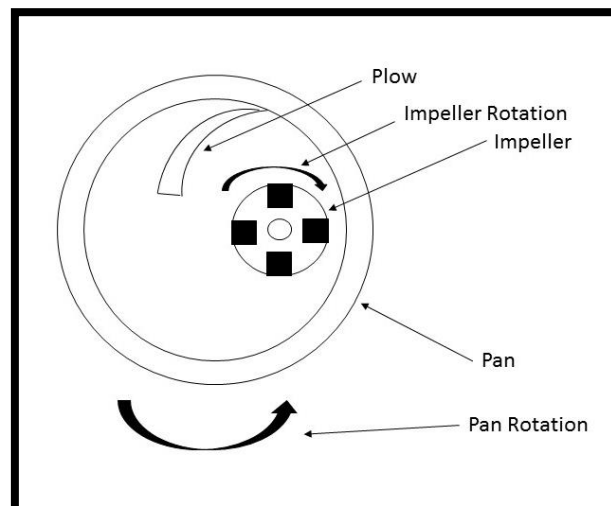
Figure 8: High intensity mixer. An impeller is rotating in the opposite direction of the pan, mixing dry powder, as well as there is a plow forcing the mix back into the mixing zone.

Mullers have been used for a long time. They can be used both for grinding and mixing, as the hardness of the material being mixed and the weight of the muller wheels will decide which situation is obtained. Soft materials will be ground, while harder materials will lose sharp edges and be rounded.

The muller wheels are usually very massive, and for ceramic applications, they are often made from iron as the weight helps to mix and grind feed batches. If iron contamination is unacceptable, stone wheels may be used, as is seen in agriculture. The pan turns in the opposite direction of the two wheels, with a plow pushing the feed out to the mixing/grinding zone [40].

3.5. Pressure Agglomeration

What distinguish briquetting from other types of agglomeration is the method of production. Briquettes are press-formed agglomerates, which apply pressure to keep larger bodies of dust agglomerated, often in combination with a binder. There are a lot of different production methods available on the market for briquetting, and in the following two sections uniaxial pressing and roll-pressing will be explained.

3.5.1. Uniaxial Pressing

Pressing is accomplished by placing powder, premixed with binder and lubricate, into a die and apply pressure to achieve compact products. Two categories of pressing are commonly used: uniaxial and isostatic. Each use powder prepared in the same manner[41].

Uniaxial pressing involves the compaction of powder into a rigid die by applying pressure along a single axial direction through a rigid punch, plunger or piston. **Figure 9** illustrates the uniaxial pressing technique. Most uniaxial presses are either hydraulic or mechanical. Mechanical presses typically have a higher production rate and are easy to automate[41]. The dimensions of the die are calculated with respect to the compaction ratio of the powder, which will give the compacted product the wanted size.
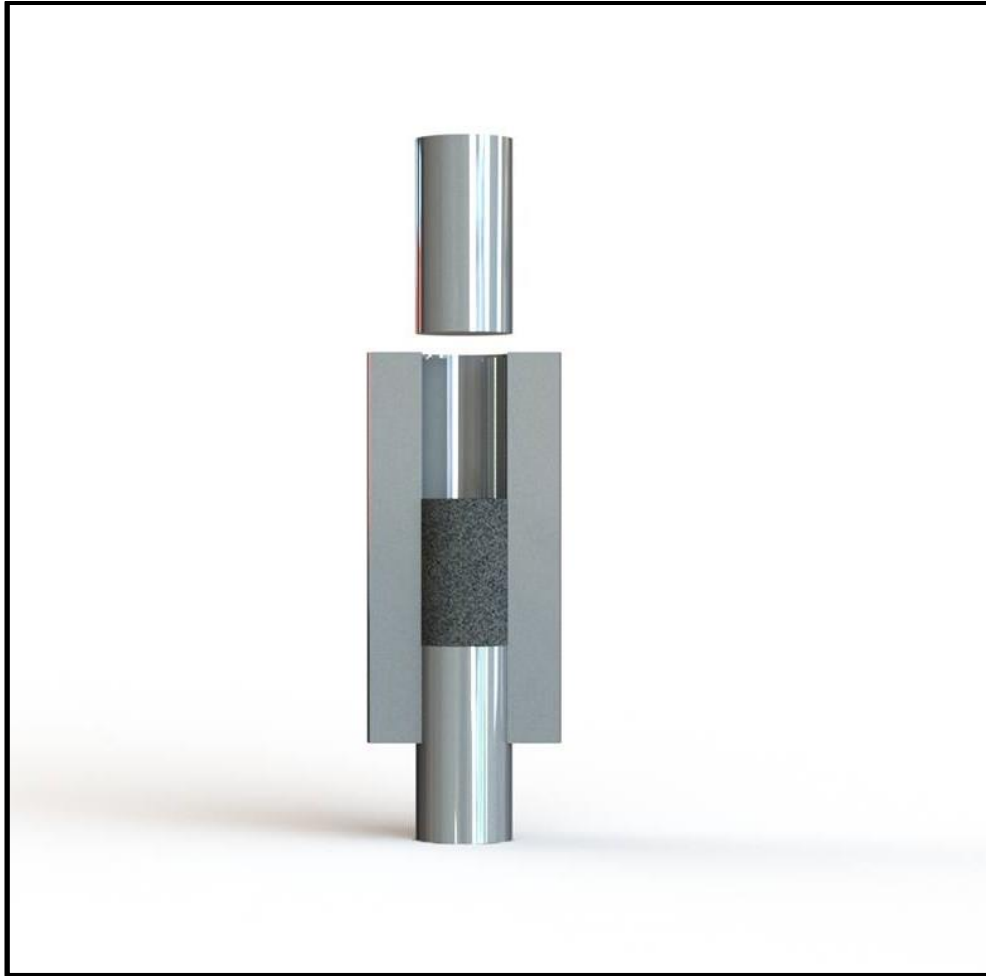
Figure 9: Uniaxial press technique. A piston is pressing the powder into the shape of the die.

Hydraulic presses transmit pressure via a fluid against a piston, and are usually operated to a set pressure, which leads to size and characteristics of the compacted product being determined by the nature of the powder, amount of die filled, and pressure applied. Hydraulic presses have a much lower cycle rate than mechanical presses[41].

Usual problems with uniaxial pressing are; improper density or size, die wear, cracking and density variation. Improper density of size is easy to observe by measuring the pressed body immediately after production. Die wear is found as the produced green bodies show slight difference in production dimensions after time[41].

Cracking is difficult to locate. It may occur due to improper die design, air entrapment, die-wall friction, die wear, or of other reasons. A crack often initiates at the top edge of the part during pressure release or ejection of the part. This can be avoided by use of lubricant to minimalize die-wall friction or by increasing the green strength through different binder selection[41].

Density variation can arise from friction between powder and die wall and between powder particles themselves. Due to this friction, large areas of the compact will experience less pressure than applied and such areas will be compacted less. Difference in pressure increase as height-to-width ratio increase. **Figure 10** shows how the external pressure is experienced throughout a uniaxial pressed powder feed. Problems due to density variation may lead to further problems in later densification steps, like firing, where low density areas will shrink

more than high density areas and thus not densifying completely and the final shape will be unsatisfactory[42].
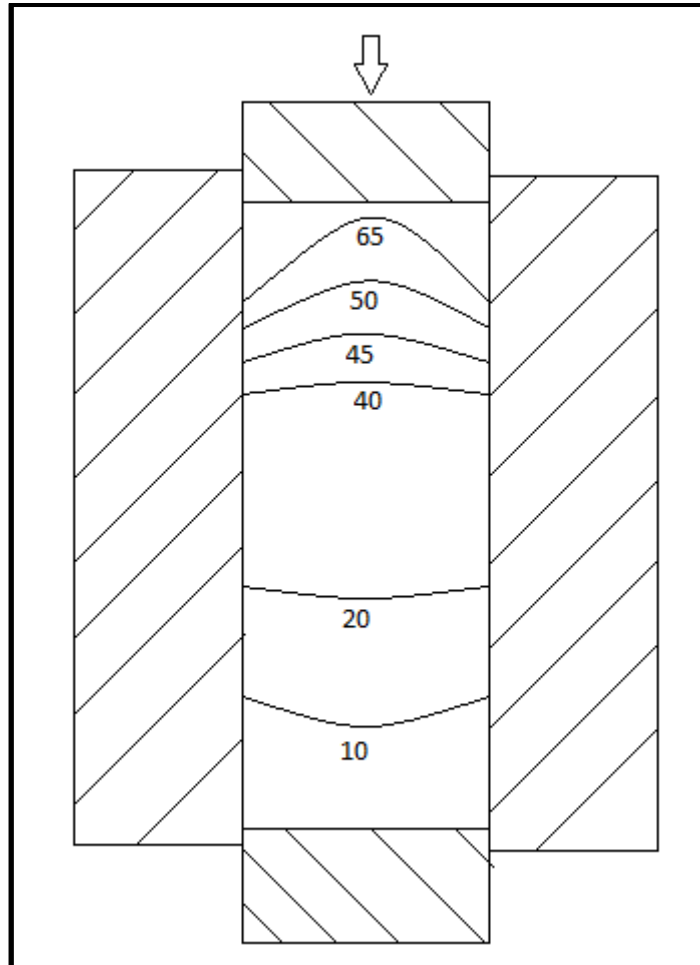
Figure 10: Pressure variation in uniaxial pressing due to die-wall friction, this leads to nonuniform pressure profile of the pressed body (Adapted from Modern Ceramic Engineering) [42]

This problem can be reduced by use of lubricant, which will lower friction. Applying pressure from both ends will reduce the problem further.

Nonuniform filling of the die is another source of density variation in green compacts. Uneven stacking causes areas with larger amount of powder to be compacted more, leading to less shrinking in these regions during later densification[42].

Presence of hard agglomerates will also result in density variation, as these act as a shield for softer powder surrounding the agglomerates, not exposing the powder to maximum pressure. Pores are then formed around the agglomerates during heat-densification[42].

3.5.2. Roll-press Briquetting

This is a continuous process where particles are fed to a machine which transports those to two rotating rolls. Each roll has one half of a die. One such roll press is shown in **Figure 11**. This shows how the particle feed is transported to the rolls, which then compress the powder and feeds out briquettes[9]. Roll pressed briquettes usually have a pillow-like shape with a low

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height-to-width ratio. The roll press is found with different feeding mechanisms, the one in **Figure 11** has a horizontal feed screw pushing the feed powder to the rolls. Other roll presses use a vertical feeding operation, where the rolls are placed beside each other and beneath the feed hopper.

1	FEED HOPPER	6	ROLLS
2	SCREW FEEDING BEARING BLOCK	7	ADAPTER
3	PADDLE MIXER	8	SHAFTS
4	HORIZONTAL FEEDING SCREW	9	BEARING BLOCKS
5	HYDRAULIC SYSTEM		
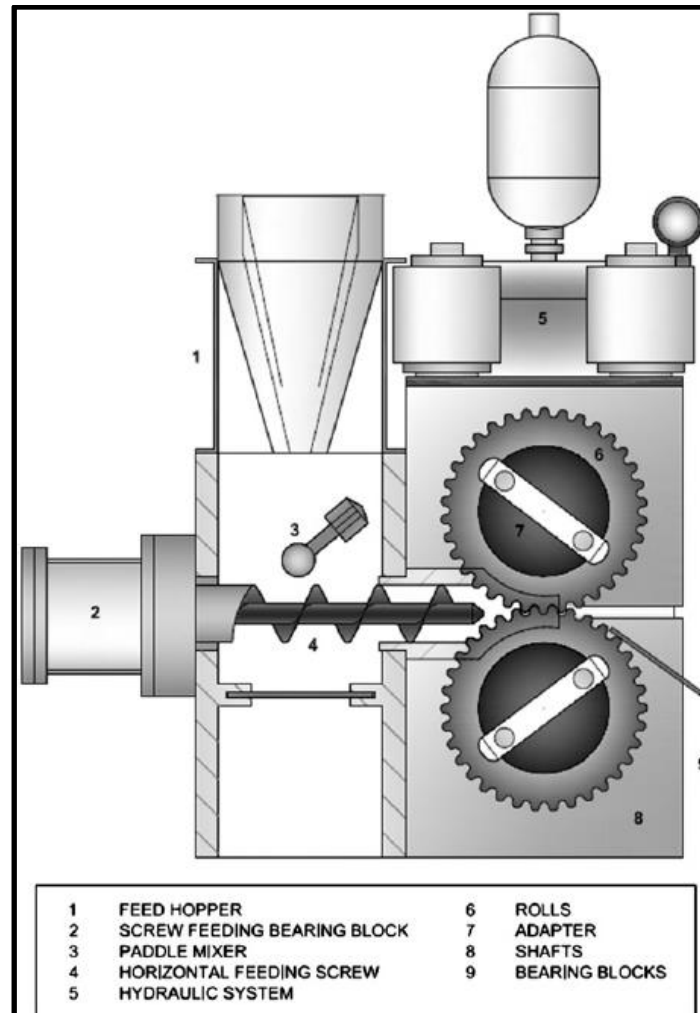
Figure 11: Schematics of roll-pressing of briquettes [43].

J. R. Johanson have posted an article in 1965 about how to optimize the running parameters of the roll press operation with regards to the maximum pressure a powder should experience [44]. These parameters are highly dependent on the material parameter *K* for a powder, called the compressibility. The compressibility is obtained from the empirical relationship between the bulk density and applied pressure of a powder and is referred to as a tablet material law (***Equation (11)***) [44, 45].

$$\frac{\sigma_1}{\sigma_2} = \left(\frac{\rho_1}{\rho_2}\right)^K \qquad\qquad (\ 11 \ )$$

In ***Equation (11)*** σ_1 and σ_2 are the maximum and minimum pressures, respectively, and ρ_1 and ρ_2 are the corresponding bulk densities.

4. Experimental

The experimental work was done following the flowsheet in **Figure 12**. It started with mixing of raw material dust, then a binder was introduced to the mix and evenly distributed. The powder-binder mixture was then immediately transported to the briquetting equipment and green bodies were produced. Two types of briquetting methods were tested: Uniaxial pressing and Roll pressing. These green briquettes were then moved to storage and tested for given time intervals after production. The next sections will describe the specifics of each step of production and testing of the agglomerated briquettes.
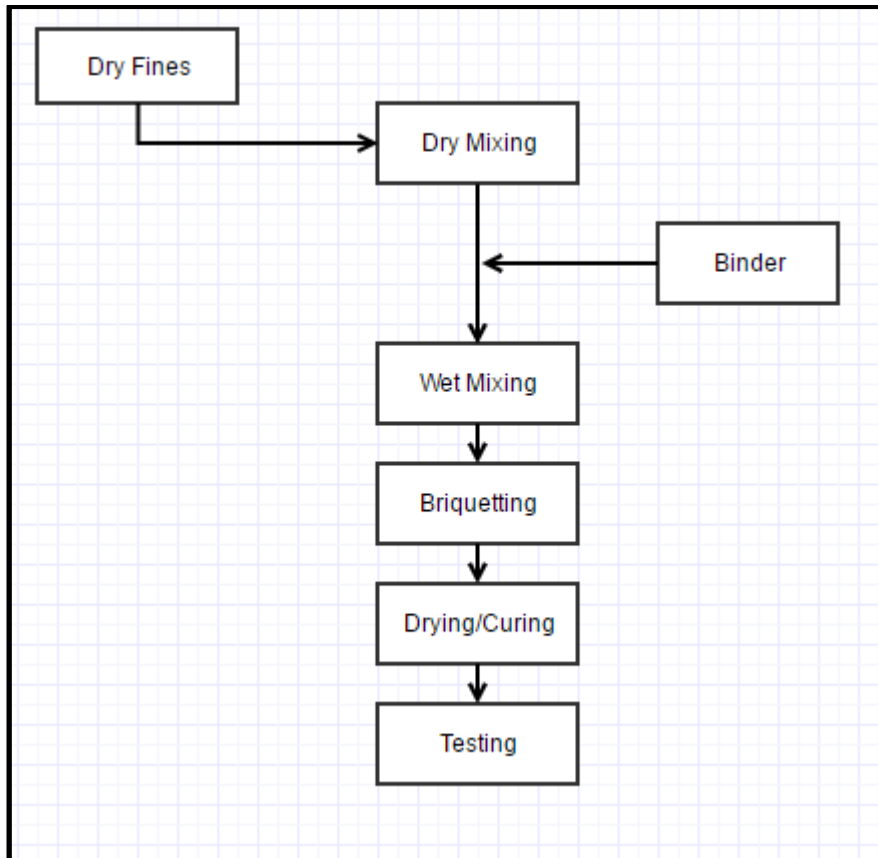
Figure 12: Flow chart of briquette production. Starting with portioning of dry fines for dry mixing, followed by binder addition and wet mixing, then briquetting, storing and testing.

4.1. Material

4.1.1. Dust Materials

The test materials were delivered by ERAMET Norway ASA. These materials were; ore fines, ore screened to be smaller than 3 mm, sludges, MOR dust, cooler dust, metallic dust screened to be less than 1 mm and environmental dust collected at plant.

The ore fines and the ore screened to be less than 3 mm in size are mostly collected around the ore crushers. Sludges arise from the off-gas cleaning facilities as one of the byproducts. MOR-dust is collected at filters above the Mn-refining unit.

For the roll press briquettes, metallic manganese fines were not included in the mix due to the high hardness of this metal and thereby the risk of heavy wear to the briquetting equipment. The metallic fines were also for the largest part close to 1mm in size, while the fines inlet to the roll press only allowed fines smaller than 0.7mm. This resolved in a higher fraction of the other dust materials, while binder was kept to the same wt% in relation to the total briquette weight.

4.1.2. Binder Materials

The binders tested in the agglomeration were; lime and molasses, magnesium-lignosulfonate and bentonite. These were used for comparison of binder efficiency. The two organic binders were also tested with different dosages. Lime and molasses was tested in dosages of 2 and 4wt%, 3 and 6wt% and 4 and 8wt% respectively. The lime used was hydrated lime $(Ca(OH)_2)$ and dissolved in water before mixing with the raw materials. The molasses was not treated in any way before mixing.

The lignosulfonate binder consists of 50% lignosulfonates and 50% water and was tested in the dosages of 4, 6, and 8wt% of total briquette weight.

One batch was made with bentonite as binder, the amount was 1wt%. Bentonite was kept dry and mixed in with the raw material dust in dry state.

The briquette batches were named based on the amount of binder used. They follow the labeling system: LxMyLzBa, where the first L represents lime, M represents molasses, second L; lignosulfonate and B; bentonite. The lower-case letters in the names denotes weight percentage of given binder. Binder compositions are given in **Table 1** below while the full compositions of the briquette batches are given in **Table 2** in the next section.

Table 1: Binder composition of the axial pressed briquettes as wt% of total briquette weight

Batch name	Binder amount in wt% of total briquette weight				
	Lime [wt%]	Molasse [wt%]	Ligno [wt%]	Bentonite [wt%]	Water [wt%]
L2M4L0B0[1]	2	4			1
L3M6L0B0	3	6			1.5
L4M8L0B0	4	8			2
L0M0L4B0			2		2
L0M0L6B0			3		3
L0M0L8B0			4		4
L0M0L0B1				1	

---

[1] Labeling system: LxMyLzBa, where the first L represents lime, M represents molasses, second L; lignosulfonate and B; bentonite. The lower-case letters in the names denotes weight percentage of given binder.

4.2. Mixing

To eliminate some of the uncertainties from the experiments, the dry raw-material mix for all binder composition briquettes was mixed at the very beginning of trials and then separated in batches for addition of binder. In that way, the difference in binder and binder dosage was believed to be the main factor contributing to change in briquette test results.

The raw material fines were mixed in dry state before any binder was added. The sludge contained some moisture and were thereby added to the mix after all the dry dust/fines were mixed together. The dry dust was mixed until achieving uniform color. When the sludges were mixed in, it agglomerated the dust into small pellet-resembling lumps. These were screened from the mix and crushed by hand, then added to the mix once more. When none of the small sludge-agglomerates were present, binder was added to the powder. Mixing was redeemed complete when no pool of liquid binder was visible and the color was uniform. The composition of each briquetting batch is shown in **Table 2**.

Table 2: Composition of briquettes. Each briquette batch follows the same ratio of dust components, the difference in amount of dust component is due to different amount of binder. The material is delivered by Eramet Norway ASA.

Axial Press	Ore dust (AF) wt%	Ore 0-3mm wt%	Sludges wt%	MOR dust wt%	Cooler dust wt%	Metallic dust 0-1 mm wt%	Environ-mental Dust wt%	Binder wt%	Sum
L0M0L4B0[2]	41.28	26.88	6.72	0.96	1.44	17.28	1.44	4	100
L0M0L6B0	40.38	26.32	6.58	1.00	1.40	16.92	1.40	6	100
L0M0L8B0	39.56	25.76	6.44	0.92	1.38	16.56	1.38	8	100
L2M4L0B0	39.99	26.04	6.51	0.93	1.40	16.74	1.40	7	100
L3M6L0B0	38.49	25.06	6.27	0.90	1.34	16.11	1.34	10.5	100
L4M8L0B0	36.98	24.08	6.02	0.86	1.29	15.48	1.29	14	100
L0M0L0B1	42.57	27.72	6.93	0.99	1.49	17.82	1.49	1	100
Roll Press									
L0M0L8B0	48.24	31.41	7.85	1.12	1.68	0	1.68	8	100
L4M8L0B0	45.10	29.37	7.34	1.05	1.57	0	1.57	14	100

[2] Labeling system: LxMyLzBa, where the first L represents lime, M represents molasses, second L; lignosulfonate and B; bentonite. The lower-case letters in the names denotes weight percentage of given binder.

4.3. Briquetting

When mixing was finished, the briquette batches were transported to the pressing tool for green body production. Two different techniques were used: Uniaxial pressing and roll pressing. These techniques are described in **section 3.5** and running parameters for this test work is found in the following sections.

4.3.1. Axial Press

Test series of all binder compositions in **Table 2** above were produced using the axial press technique. They were produced in a die of stainless steel with an accompanying piston. The die was filled to the top with the powder and binder mixture, then the piston was placed on top and a compression tool was used to apply force. The compression tool used was manually run and the briquettes were produced with a force of 10kN, each briquette held at that pressure for 30s. The size of the briquettes was 30mm in diameter and 21-22mm in height. **Figure 13** shows one of the axial press formed briquettes produced with 6wt% lignosulfonate as binder.
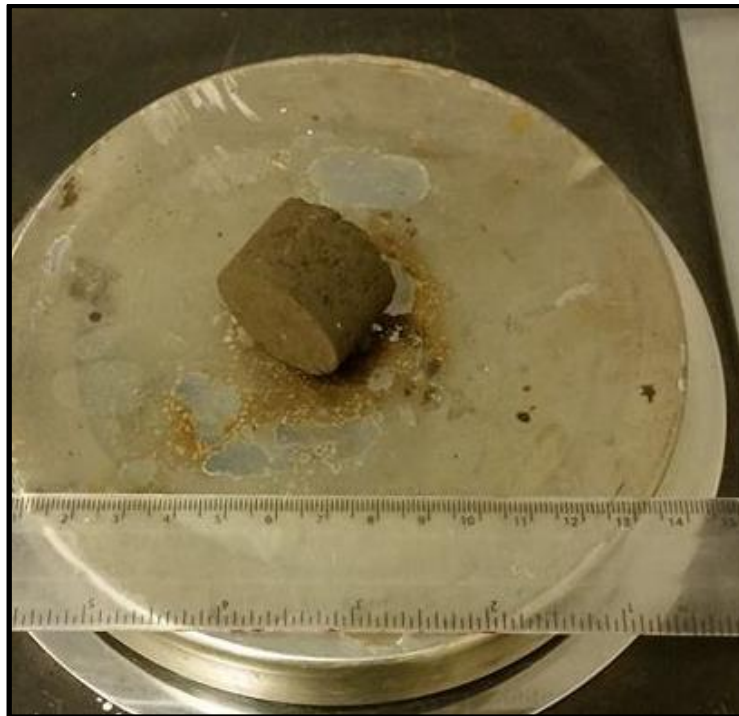
Figure 13: Briquette made with 6wt% Lignosulfonate. Diameter 30 mm, height 21 mm

As means to compare different binders for briquetting of manganese ore fines, the binders lime and molasses, lignosulfonate and bentonite were used. For the two organic binders, three batches were made with different amounts of binder. The different batches are given in **Table 2** above. Briquettes were made for drop tests and compression tests. More details of these test regimes are given in the specific **Sections 4.4** and **4.5**.

In addition to the briquettes described above, there were made one briquette series from each binder type which were to be stored and drop tested once every week for 5 weeks in total. This to see how the different binders are affected by storage time. The batches made for the

long term-test were L3M6L0B0 (3wt% lime and 6wt% molasses), L0M0L6B0 (6wt% lignosulfonate) and L0M0L0B1 (1wt% bentonite).

4.3.2. Roll Press

Two batches were produced with the roll press briquetting machine Briketta, provided by SINTEF Materials, Trondheim. The test batches made in the roll press were L4M8L0B0 (4wt% lime and 8wt% molasses) and L0M0L8B0 (8wt% lignosulfonate), after showing best promise of the axial pressed briquettes. These briquettes were made for drop test and compression test application, as well as compression test after heat treatment. As mentioned in the mixing chapter, metallic fines were not part of the batches made with this method. **Table 3** shows the test parameters of the machine during briquetting.

Table 3: Running parameters of the Briketta during briquette production.

Feed Screw Torque	5.3 [Nm]
Feed Screw Speed	38.2 [RPM]
Roll Torque	125 [Nm]
Roll Speed	2.8 [RPM]
Agitator Torque	1.3 [Nm]
Agitator speed	8.6 [RPM]
Roll Gap	0.7 [mm]
Roll Force	28.5 [kN]

4.4. Compression Test

The force needed to create a crack propagating through the surface of the briquette, in [N], was noted as the maximum compression strength of the briquettes. This test was set to stop when the force applied to a briquette dropped by 25% of the maximum measured force during a run. The compression machine held a constant speed of 2mm/min during the run. The machine used for compression testing was the Zwick Roell 72.5 Tensile test equipment.

Test series for compression test consist of five briquettes of each test batch. Briquettes were tested one day and two days after being produced. **Figure 14** shows a simplified set-up of the basic principal of the compression test.

From the roll-press series, briquettes went through different heat treatments prior to compression test in addition to being tested in green state after one and two days of storage. More details of the heat treatments are found in **Section 4.6**.
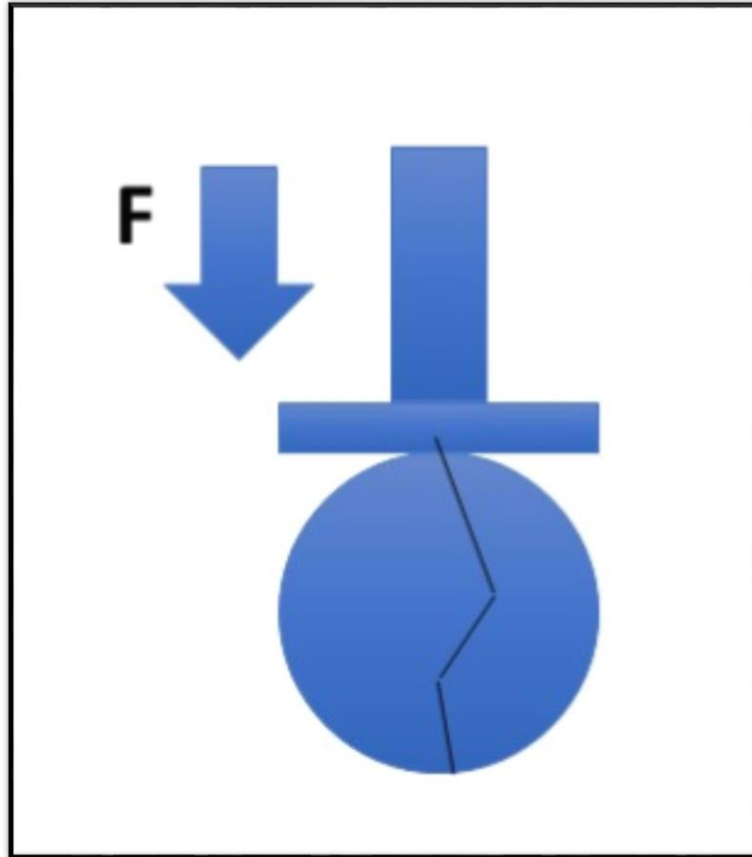
Figure 14: Representation of the compression strength test. The briquette is placed beneath a piston which moves at a constant speed while measuring the force needed to maintain that speed.

4.5. Drop Test

The drop test was executed by dropping each test briquette two times from a height of 2m onto a steel plate. Briquettes are dropped through a pipe wide enough to not touch the pipe wall while falling. The briquettes were then screened by sieves with square grid sizes of 10mm, 6.3mm, 3.15mm, 2mm and 1mm as means to find the degradation from falling and amount of different sized fines produced from the impact.

Test series for the drop test consists of four briquettes for each test. Briquettes were tested 1 day and 2 days after production.

In addition, one long-term test batch was made from each binder type, 3 series in total. These were tested once every week after production for a total of five weeks. The intention of the weekly test is to investigate the evolution of strength of the briquettes over time. The storage environment was dry and at room temperature.

The original long-term storage batch of lime and molasses broke after one week of storage. This led to leftover roll press briquettes from the 4wt% lime and 8wt% molasses batch being tested for drop strength after 5 weeks of storage.

Experimental

4.6. Heat Treatment

The briquettes made from the roll press were treated at different temperatures prior to compression testing. Briquettes were heated to 105°C, 300°C, 500°C and 800°C respectively at a heating rate of 10°C/min, then held at the given temperatures for 1h. The 105°C treatment was done in a drying cabinet; the other three temperature treatments were performed in a Nabertherm N 30/85 NA muffle furnace. This test regime was done for the 8wt% lignosulfonate and 4 and 8wt% lime and molasses batches made from the roll press to investigate the strength development of heated briquettes. 10 briquettes from each batch were treated at each of the given temperatures.

4.7. Reference Ore

Manganese ore lumps were tested as a reference to the briquettes. The ore lumps were sized to approximately the same weight as the axial pressed briquettes, then drop test and compression test was performed in the same manner as for the briquettes. The type of manganese ore used as reference to the briquette results is kept confidential due to external considerations.

4.8. Summary of Experimental

In **Table 4** is a summary of which tests has been performed on each binder combination briquette.

Table 4: Summary of which tests have been performed with what batches

| | Axial press | | | | | | | Roll press | |
	L0M0L4B0[3]	L0M0L6B0	L0M0L8B0	L2M4L0B0	L3M6L0B0	L4M8L0B0	L0M0L0B1	L0M0L8B0	L4M8L0B0
Briquetted	x	x	x	x	x	x	x	x	x
Drop test 1 and 2 days storage	x	x	x		x	x	x	x	x
Compression 1 and 2 days storage	x	x	x		x	x	x	x	x
Long term storage and drop test		x					x		x
Macro imaging	x	x	x			x	x	x	x
Heat treatment and compression								x	x

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[3] Labeling system: LxMyLzBa, where the first L represents lime, M represents molasses, second L; lignosulfonate and B; bentonite. The lower-case letters in the names denotes weight percentage of given binder.

5. Results

Results from the experimental procedures describe in **Chapter 4** are presented in the following sections. The set-up of this chapter is divided in observations from: Mixing, briquetting and structure, strength test results (axial press and roll press results are separated), heat treatment results and reference ore test results.

5.1. Mixing

5.1.1. Raw Material

Table 5 contains a list of observations of the raw material fines used for agglomeration. The overall mixing of these fines was easily managed, but the semi-dry sludge tended to create small pellet resembling agglomerates while mixed with the rest of the fines. To avoid these pellets, they were screened out from the mix by a 2mm sieve and crushed by hand before re-added to the mixture. The raw material mix was considered well mixed when these pellets stopped forming and the color of the mix was uniform.

Table 5: Observations from the fines used for agglomeration

Type of fines	Observations
Ore dust as fines	Black color, dry. Easy to portion out
Ore screened to 3-0mm	Black color, dry. Easy to portion out
Sludges	Gray color, semi-wet clay-like structure. Very adhering to itself and other surfaces. Hard to portion out
MOR-fines	Rusty brown color, dry. Easy to portion and handle
Cooler dust	Light brown color, dry. Easy to handle and portion out
Environmental dust	Light brown color, dry. Easy to handle and portion out
Metallic fines	Metallic gray color, contained some moisture. Easy to portion and handle

5.1.2. Binder

Axial Press

Table 6 presents a summary of observations made of the binder properties. Mixing the hydrated lime with water was done without any problems, but the molasses was a highly viscous fluid which is very adhering. The lignosulfonate mixed with 50wt% water had a viscosity similar to water and was rather easily handled and homogenous. The bentonite was a dry binder material in powder form with particle size smaller than 0.5-1mm. This powder was highly manageable and easily mixable.

Table 6: Comparison of binder behavior

Binder type	Number of components and composition	State when mixed	Comments
Lime and molasses and water	3 (31-62-7 wt%)	Wet	High viscosity, very adhering
Lignosulfonate and water	2 (50-50 wt%)	Wet	Low viscosity, close to water in behavior
Bentonite	1	Dry	Easily managed, dry powder

Lime and molasses: The hydrated lime was dissolved in water, then mixed with molasses. This lime and molasses mixture had highest viscosity of the two liquid binders used. It was not a problem adding it to the raw material mix, if the mixer was running simultaneously.

With 2wt% lime and 4wt% molasses, the binder did not appear to completely wet the powder, as the mix was still quite dry after the addition of binder. Briquettes were produced, but none of them made it through transportation from the laboratory to the storage room. This fines/binder ratio was made three times, but all with the same result.

3wt% lime and 6wt% molasses did look promising after the mixing procedure. The mix looked moister than the previous batch as the color was darker than before addition of binder. Some smaller agglomerates were produced while mixing, but these were crushed and further mixed. Small dust particles escaped to the air when changing storage container after the mixing process.

4wt% lime and 8wt% molasses showed good wetting of the dry fines and created a semi-sticky mixture of particles.

Lignosulfonate: The lignosulfonate/water binder had a viscosity very like water. Addition of binder to the dry fines mixture was unproblematic and the binder spread fast and evenly into the dry fines.

4wt% lignosulfonate added a bit of moisture to the mixture, but it was still quite dry. Dust was still rising from the mixer after binder was fully mixed in.

<u>Results</u>

6wt% gave a more distinct change in moisture of the dust-binder mixture and no dust was leaving to the ventilation after binder addition.

8wt% gave much the same visible result as for 6 wt%, no dust entering the ventilation after complete mixing and visibly wet fines.

Bentonite: As this binder was added in dry state, it was very easy to handle, but it was rather difficult to decide when the mixing was complete. When none of the bentonite particles were visible, it was considered mixed properly.

Roll Press

The mixing of the two roll press briquetting batches, 4wt% lime and 8wt% molasses, 8wt% lignosulfonate, was performed without the metallic fines for the reasons stated in **Section 4.1.1**. It gave the same observations as for those made for the axial press with the same binder amount.

5.2. Briquetting

5.2.1. Axial Press

The axial press technique produced briquettes like the one made with 6wt% lignosulfonate in **Figure 15** below. They have a cylindric shape with a diameter of 30mm and a height of 21-22mm. The weight of the briquettes ranged from 35-41g in the batch of 6wt% lignosulfonate. After this batch, the die had to be changed, and the height decreased to 17-18mm of the green briquettes, and the weight to around 25g. The average density before pressing was 1.8g/cm^3, and after pressing at 10kN was 2.6g/cm^3. During briquetting in the axial press, heavy abrasive wear was observed on the die and piston. It was believed to arise from the hard manganese metal fines.

Figure 15: Briquette made with 6wt% Lignosulfonate. Diameter 30 mm, height 21 mm

Results

Lime and molasses: Briquetting of the lime and molasses binder batches was in general no problem, the fines/binder mix was compressed and created products of wanted geometry. Specifics about each batch is further elaborated in the following paragraphs.

The 2wt% lime and 4wt% molasses binder/powder mixture was as stated in the previous section still very dry, even after binder addition. The briquettes were produced and kept intact at the beginning immediately after production, but when they were transported to the storage room, they broke. This batch was attempted to make three times, but the result was the same for each try, the briquettes broke during transportation.

The 3wt% lime and 6wt% molasses briquettes were produced with no problem. They tolerated the transport to the storage room without receiving any visible damage, such as cracks or crumbling from the edges.

The 4wt% lime and 8wt% molasses fines-binder mixture was moist when briquetted and the process of production was done without any difficulties. They were transported to the storage room without any visible damage.

Figure 16 is a macro picture showing the surface of the 4wt% lime and 8wt% molasses briquettes. The orange particles are MOR-dust, rich in iron oxide. Visible are larger particles embedded with smaller particles filling the voids. Some small cracks and voids are visible around the largest particles on the surface.
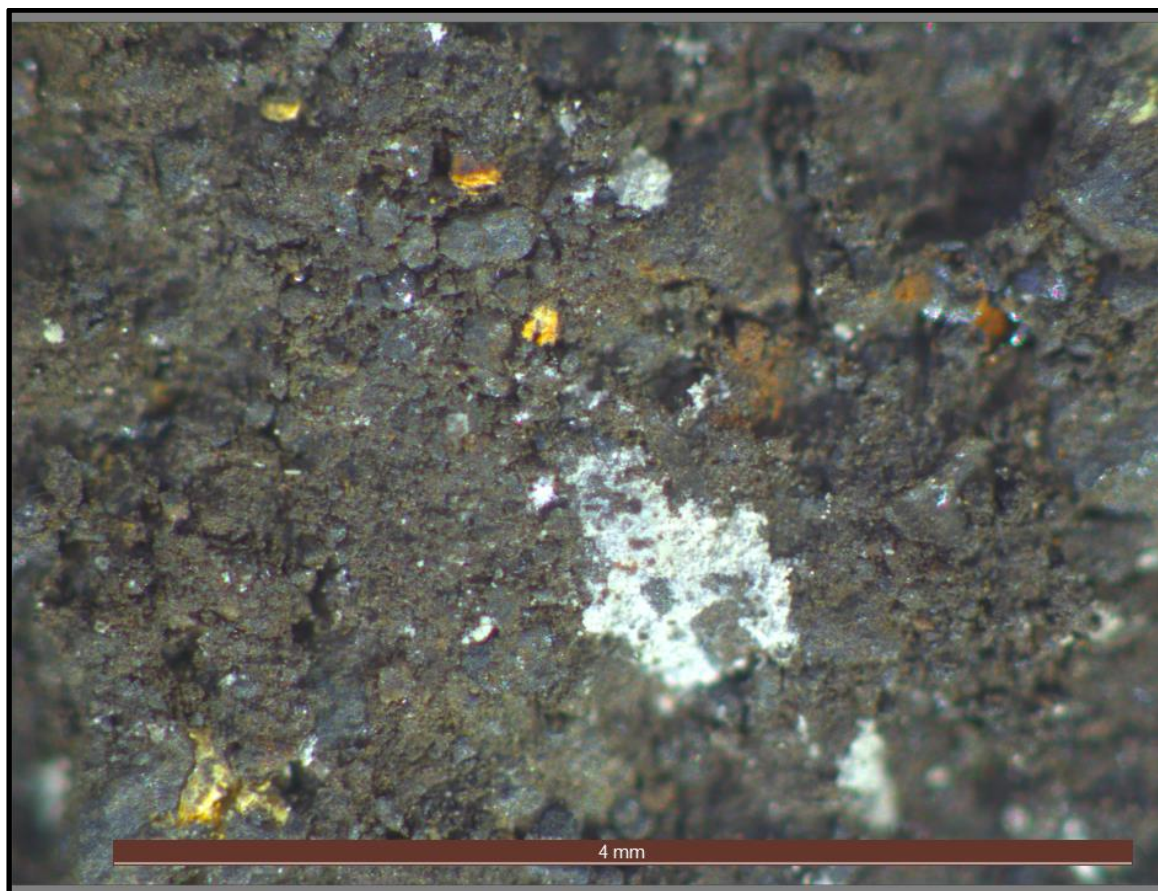
Figure 16: Picture of the surface of 4wt% lime and 8wt% molasses. Some smaller voids and cracks are visible around the larger particles of the briquette.

Lignosulfonate: The lignosulfonate binder had a good moistening effect of the dry dust and in general briquetting of all three lignosulfonate batches was done without any difficulties.

The 4wt% lignosulfonate mixture was, as stated in the mixing section (**Section 5.1**), quite dry, but briquetting was no problem and the briquettes seemed more wet after pressing than the mixture did before. There were some dust escaping to the air when pouring the mixture into the die, but after transportation to the storage room there was no damage observed.

6wt% lignosulfonate was very like the 4wt% lignosulfonate, but there was no dust escaping to the air while pouring this mixture into the die. Transportation gave no visible damage to these briquettes.

For the 8wt% lignosulfonate briquette batch, it was the same as for the 6wt% lignosulfonate. The dust-binder mixture was moist, but not as sticky as the 4wt% lime and 8wt% molasses, and briquetting was problem free. These briquettes had a glossy and moist surface and left little dust on the gloves when handled. The briquettes made it through transportation to the storage room without any visible cracks or other surface defects.

Figure 17 shows a macro image of the surface of one of the 4wt% lignosulfonate axial pressed briquette. From this image, it is seen how the smaller particles are spread around the larger ones. One larger area containing orange MOR-dust is seen in the middle of the image as well. Macro images of the other lignosulfonate briquettes are attached in the appendix.
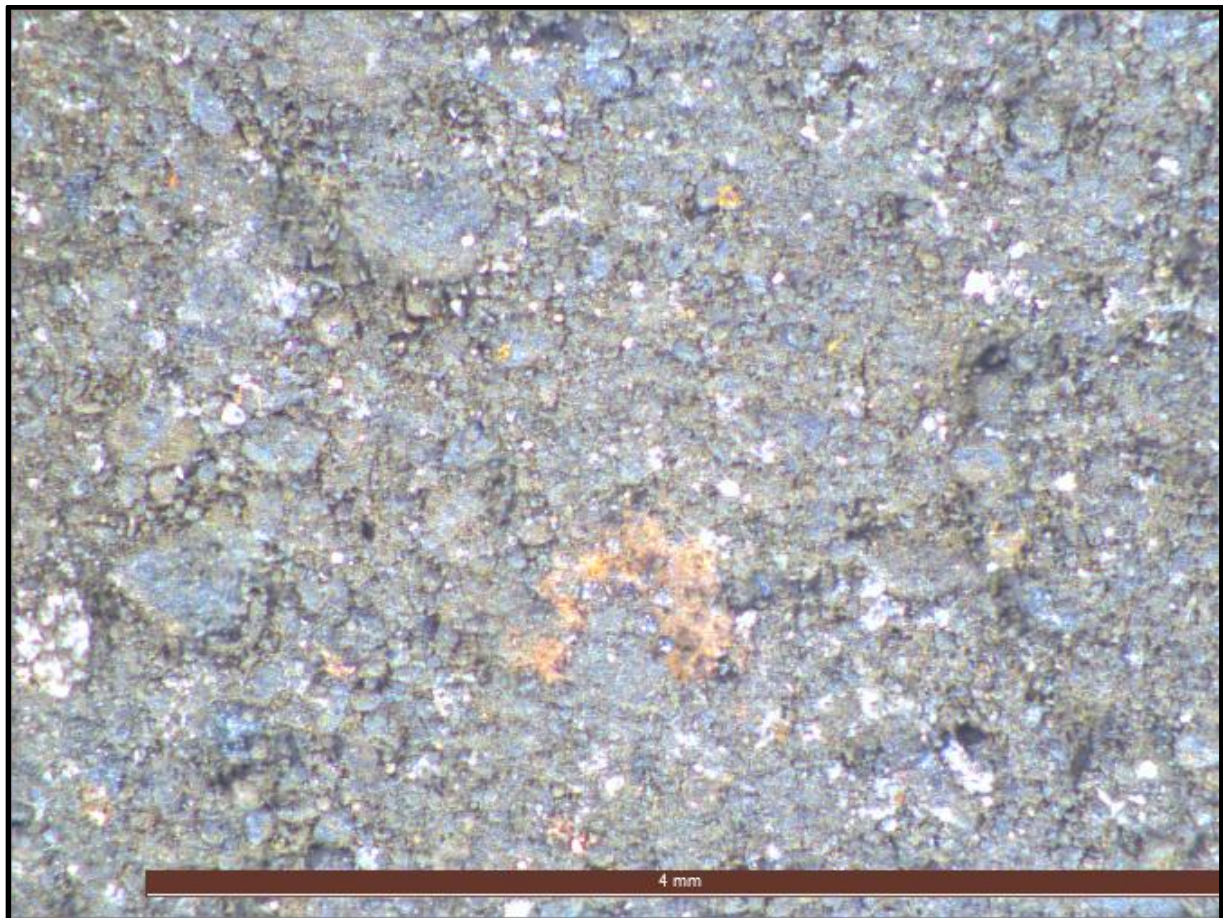
Figure 17: Image of the surface of a 4wt% lignosulfonate briquette.

Bentonite: The 1wt% bentonite binder mixture was dry, as no moisture was added in the mixing process. Briquetting was done without any difficulties, but a lot of dust was produced around the work space while making these briquettes. The finished briquettes had smooth surfaces and the edges were complete. Transportation from the laboratory to the storage room gave no damage to these briquettes. From **Figure 18**, several small cracks can be observed on the surface of the 1wt% bentonite briquette, more than for any other of the briquette types.
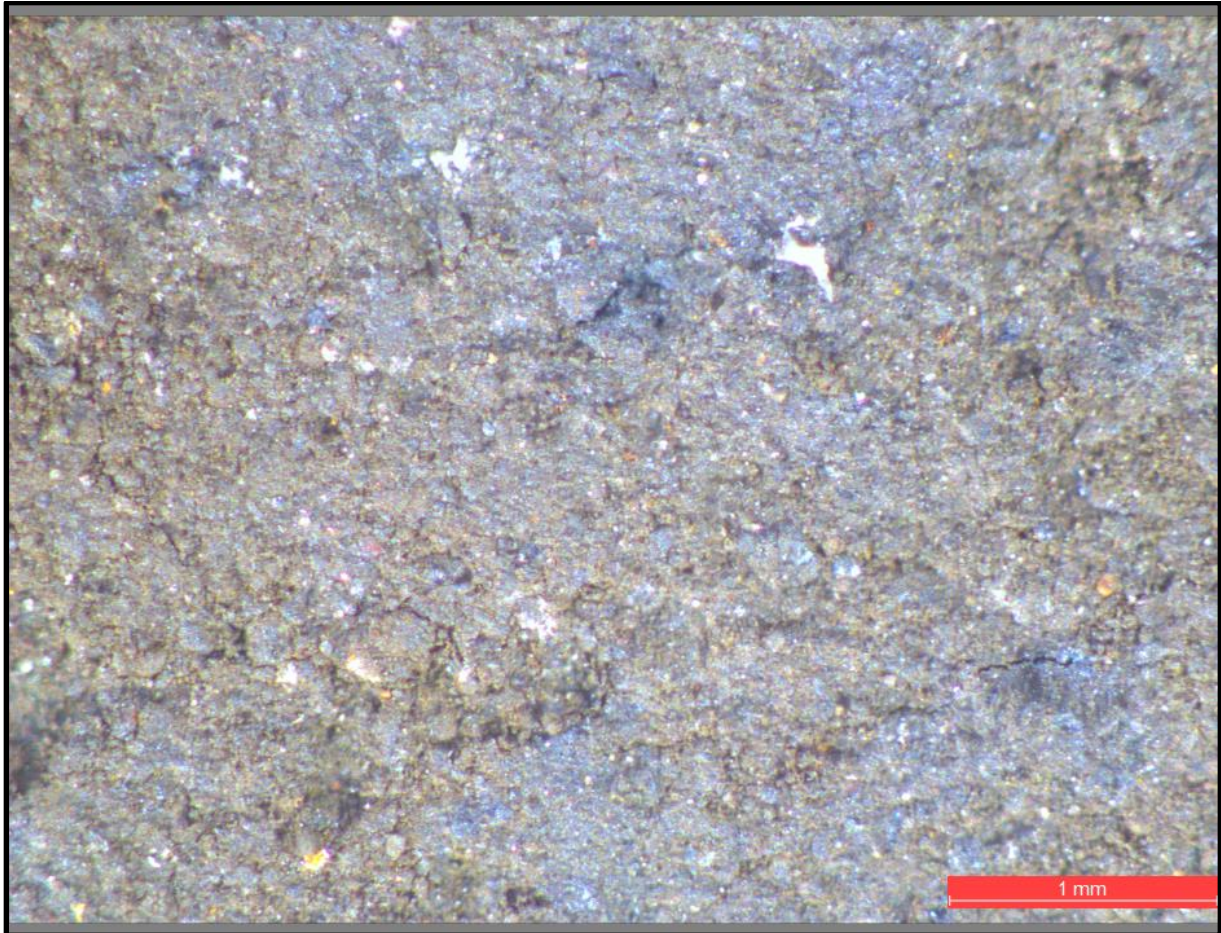
Figure 18: Macro image of the surface of 1wt% bentonite briquette. There are several small cracks on the surface of this briquette.

5.2.2. Roll Press

The roll press briquetting was much faster than the manual axial press method. The fines/binder mixtures were fed at the top of the machine, then pushed constantly down to the feed screw. The first and last few briquettes produced per batch were not compacted desirably due to low powder mix pressure from the feed screw to the press, but the briquettes made in between had a smooth surface and were well compacted (**Figure 19**).

The machine produced batches from 1 kg of fines/binder mixture at a much higher rate than the axial press used and the number of briquettes in such a batch was about 90 good briquettes. The briquettes were quite small, 1.5 cm length and 1 cm height, giving an even force distribution in the green body.

Results

Figure 19: Picture of the briquettes produced with Briketta from the 8wt% lignosulfonate batch.

Lime and molasses: One roll press batch was made with the binder limestone and molasses, at the relative amount of 4wt% and 8wt% respectively of the total batch weight. This batch was made without the metallic fines, due to the risk of intense wear of the briquetting equipment. The briquettes made in the middle of production had a smooth surface and no defects were visible. Those made at the very beginning and end were sorted out from the rest during production. Those briquettes had large defects, such as not the correct shape, they were cracked and were visibly not densified to the desired degree.

Lignosulfonate: One roll press batch was made with the lignosulfonate binder with the briquetting roll press. This was a batch with 8wt% lignosulfonate and no metallic fines, as explained in **Section 4.1.1**. These briquettes had a smooth, round surface and none from the middle of production had visible flaws, such as surface cracks. The briquettes made at the very beginning and end of the batch had the same defects as the lime and molasses briquettes described in the paragraph above and were sorted out during production.

In **Figure 20** on the next page is a macro image of the surface of one roll pressed 8wt% lignosulfonate and one 4wt% lime and 8wt% molasses briquettes. Due to the curvature of the briquette it was not possible to have the whole image in focus, but from the image, it is visible that these briquettes are more compacted than the axial pressed briquettes. There are less tops and valleys on the surface than for the axial pressed ones.

Results
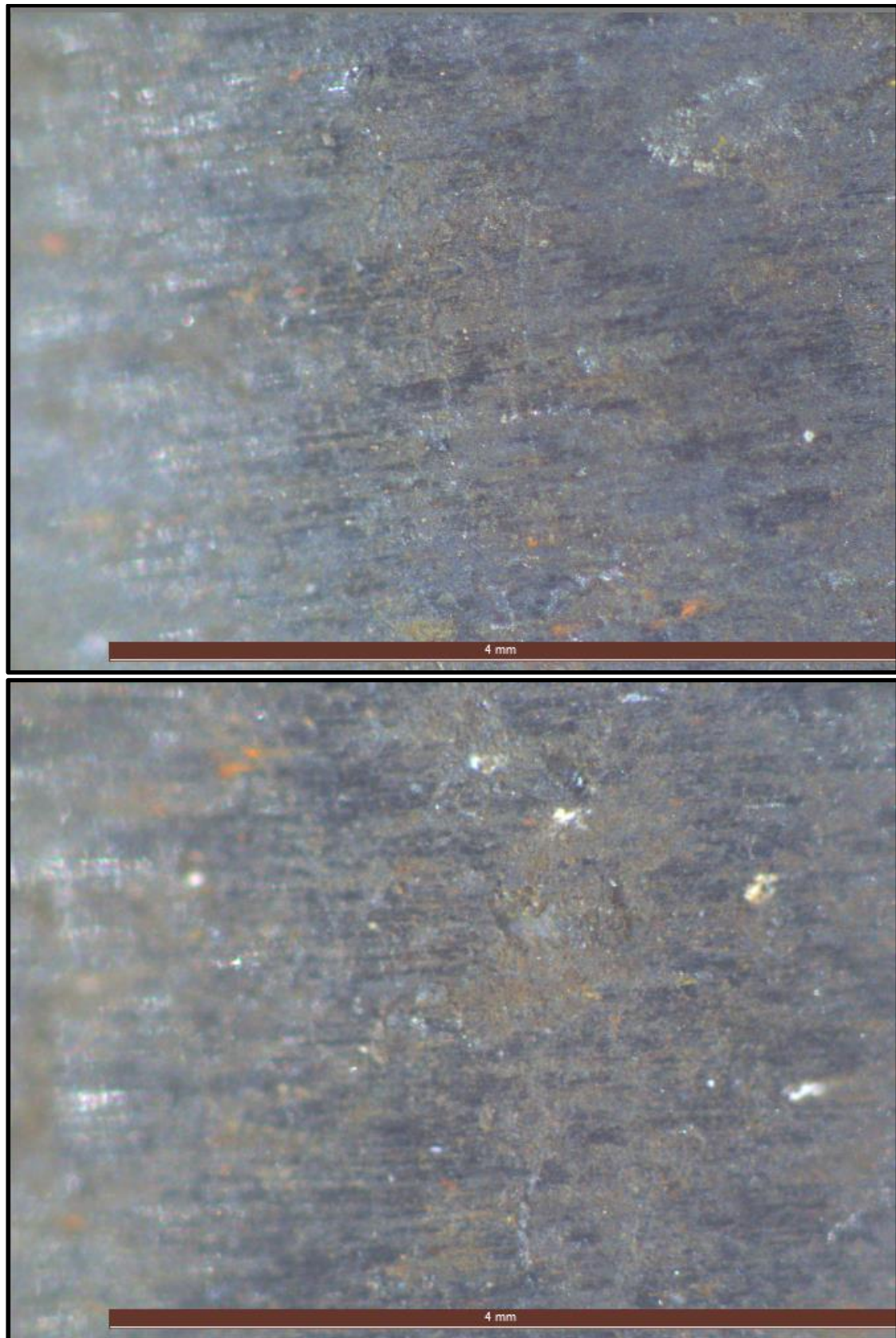
Figure 20: Macro images of the surface of roll pressed briquettes. Top: 4wt% lime and 8wt% molasses. Bottom: 8wt% lignosulfonate.

Results

5.3. Strength Test Results

5.3.1. Axial Pressed Briquettes

Compression

Table 7 presents the compression test results of all the tested batches. The 2wt% lime and 4wt% molasses was not tested due to not being strong enough to handle transport to the storage room. When the briquettes were compressed, all showed the same fracture pattern, which is represented both in **Figure 14** and **Figure 21**. They broke through the middle in a zig zag patter, and some fines were loosened from the green bodies. Specifics of each batch are given in the following paragraphs.

Table 7: Results from compression of axial pressed briquettes. Average of 5 briquettes per test.

	Breakage force after 1 day of storage [N]	Breakage force after 2 days of storage [N]
L2M4L0B0[4]	------------	-----------
L3M6L0B0	51.8 ± 13.7	35.8 ± 9.4
L4M8L0B0	55.8 ± 9.7	89.6 ± 11.9
L0M0L4B0	28.4 ± 6.1	31.9 ± 2.9
L0M0L6B0	61.6 ± 10.6	51.4 ± 9.0
L0M0L8B0	80.0 ± 13.2	59.0 ± 6.0
L0M0L0B1	54.0 ± 9.7	56.7 ± 7.5
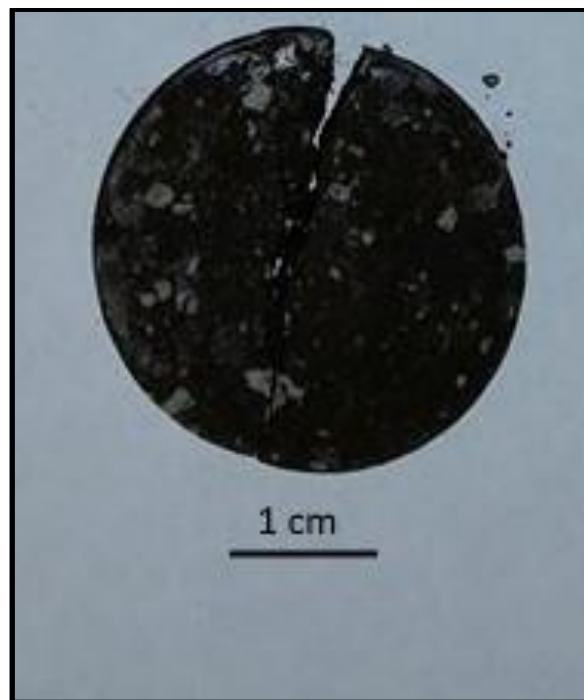
Figure 21: Fracture pattern of a compression tested sample
(Lime and molasses 4 and 8 wt%)

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[4] Labeling system: LxMyLzBa, where the first L represents lime, M represents molasses, second L; lignosulfonate and B; bentonite. The lower-case letters in the names denotes weight percentage of given binder.

Lime and molasses: Starting with the test results from the three batches with lime and molasses (2+4wt%, 3+6wt% and 4+8wt%) that were tested in compression strength, there was some spread in the results. As mentioned, the batch with 2wt% lime and 4wt% molasses was not strong enough to be transferred from the axial press to the storage room, so no values of strength were possible to measure for this batch.

The two other batches were possible to test, as no damage occurred during transport. The results are numerically presented in **Table 7** and shown graphically in **Figure 22** below. From these results, the batch with the highest amount of binder produce the strongest briquettes. The same is true in the drop test of these axial pressed briquettes. The results show that the 4 and 8wt% lime and molasses strengthened with time from one to two days of storage, while the 3 and 6wt% weakened. The compression strength after one day of storage is also much the same for these two batches.
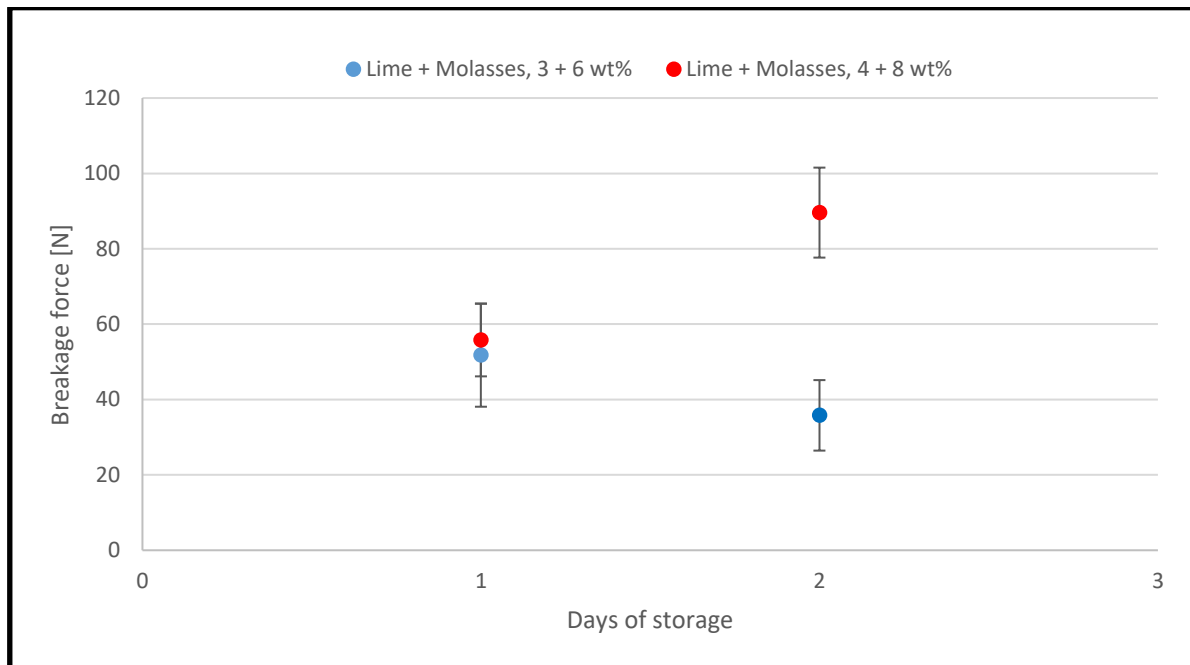
Figure 22: Compression test results for 3 and 6wt%, and 4 and 8wt% lime and molasses axial pressed briquettes after one and two days of storage.

Lignosulfonate: Three different dosages of lignosulfonate was tested with the axial press method. These (4wt%, 6wt% and 8wt%) was successfully transported to the storage room and compression testing was performed according to the test schedule given in **Section 4.4**. The results are given in **Table 7** and a graphical comparison is shown in **Figure 23** underneath. The same holds true for lignosulfonate as for lime and molasses; increased amount of binder increase the compression strength of the agglomerate. The results also show that the 6 and 8wt% lignosulfonate decrease in strength from one day of storage to two days, while the 4wt% has a slight increase in strength. The standard deviation lowers from day one to day two for all batches.
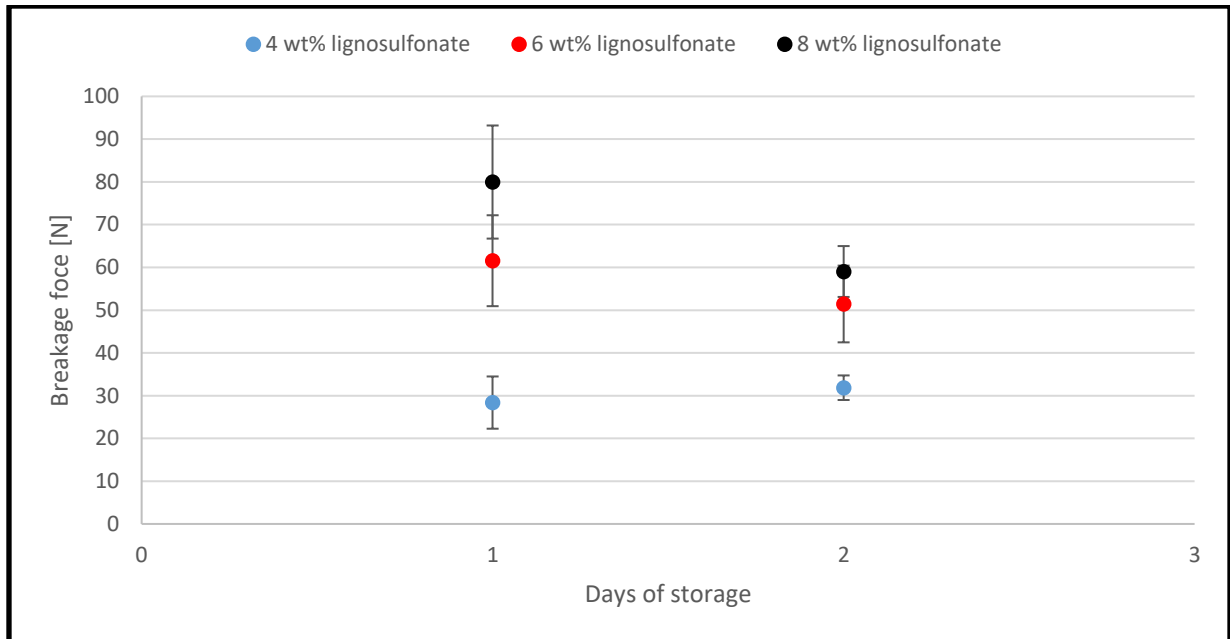
Figure 23: Compression test results of 4, 6 and 8wt% lignosulfonate axial pressed briquettes after one and two days of storage.

Bentonite: The bentonite briquettes was transported successfully from production to storage, and compression test was completed according to the test schedule in **section 4.4**. The compression test results after one and two days of storage are shown in **Figure 24**. There is no real change in strength going from one to two days of storage, and it is close to the 6wt% lignosulfonate briquettes.
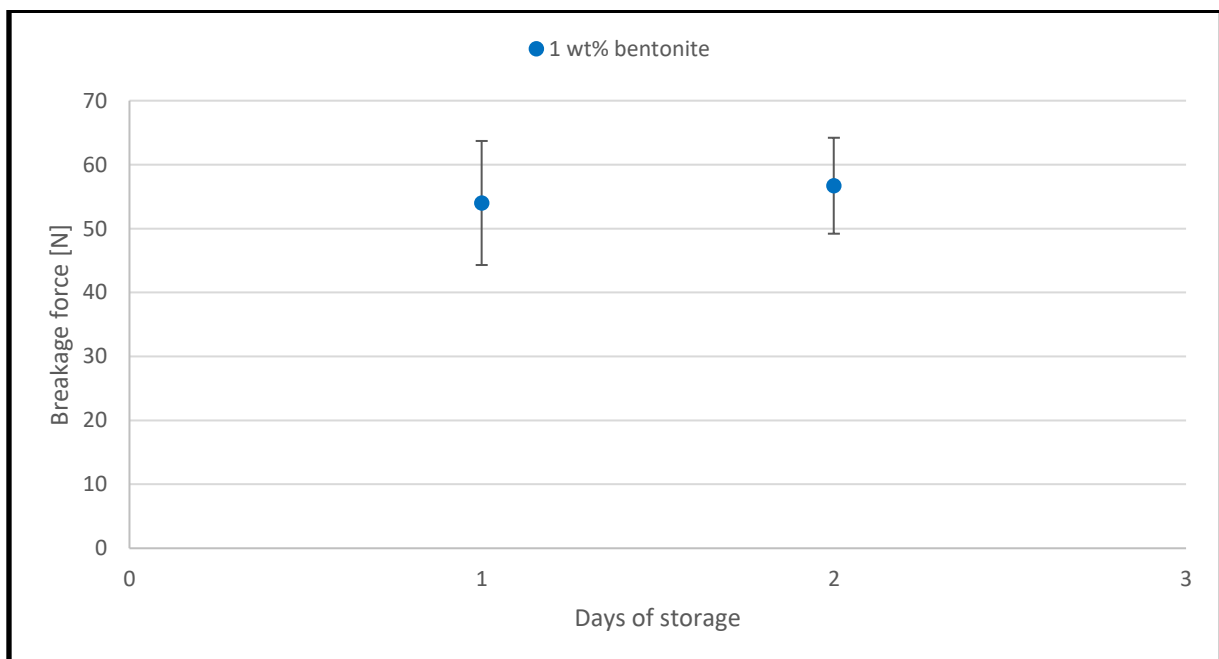
Figure 24: Compression test result of the 1wt% bentonite axial pressed briquettes after one and two days of storage.

Results

Drop strength

Drop tests were performed according to the schedule described in **Section 4.4**. The drop test results are given in the following paragraphs. Each result is given as the average of 4 dropped briquettes. The accumulated screening analysis's given in this section represents the amounts of fines held at each given screen, accumulated from the left. The difference between the given points is the amount of fines found held at the larger screen.

Lime and molasses: As the 2wt% lime and 4wt% molasses composition briquettes did not tolerate the short transportation from the pressing laboratory to the storage room, no drop test results were acquired.

The drop test results from the 3wt% lime and 6wt% molasses is shown in **Figure 25**. As can be seen, this briquette batch creates a lot of dust during drops from a 2m height. 50% of the total briquette weight is concentrated in fines smaller than 1mm. There is no real difference in results from one to two days of storage for this batch, contradicting the negative change shown in the compression test.

Drop test of the 4wt% lime and 8wt% molasses yielded the results given in **Figure 25** underneath. It shows that after one day of storage, approximately 54wt% of the briquette is above 3.15mm in size after two drops, while after 2 days, approximately 74wt% of the briquette is found as pieces larger than 10mm in size. It shows a clear increase in drop strength from one to two days.

One observation from the drop test of 4wt% and 8wt% was that one of the briquettes dropped did not break, but instead was deformed. **Figure 26** shows this deformed edge.
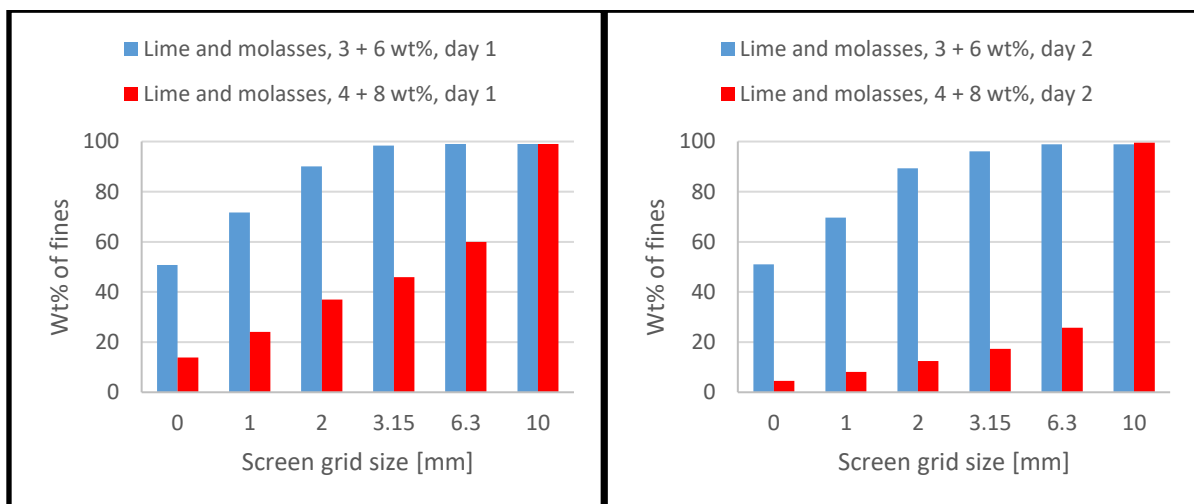
Figure 25: Screening analysis accumulated from the left from drop test of the 3 and 6wt%, and 4 + 8wt% lime and molasses binder briquettes produced in the axial press. Left: One day of storage. Right: Two days of storage.
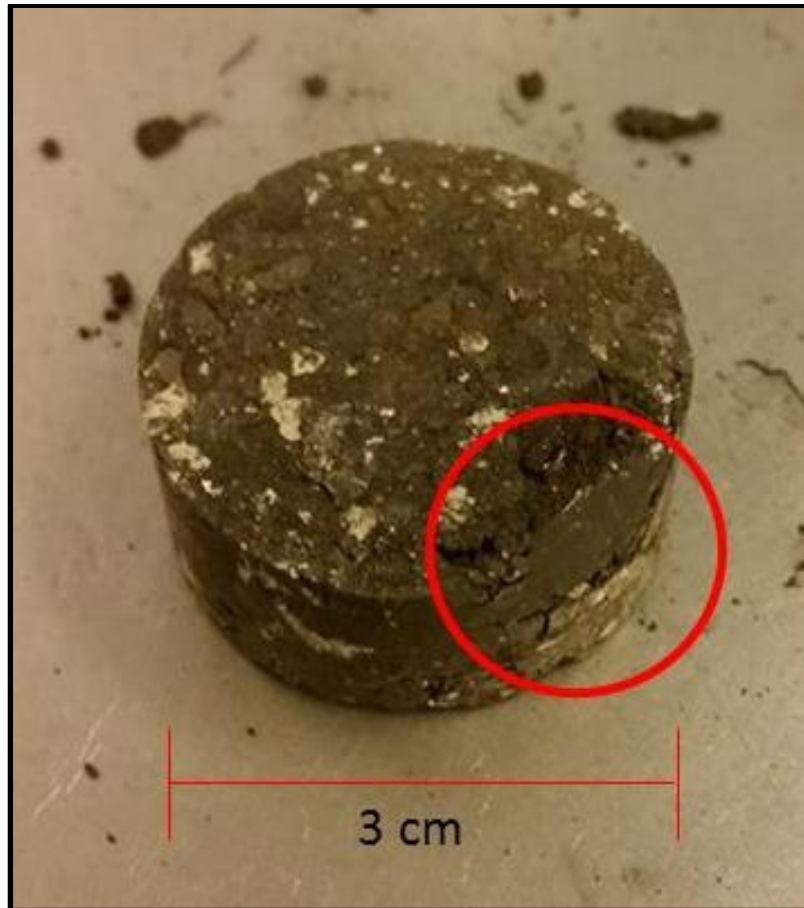
Results

Figure 26: 4 and 8wt% lime and molasses briquette after one drop. The edge marked with a red circle has been deformed.

Lignosulfonate: The drop test results from the briquettes produced with lignosulfonate is given in the following section. The 4wt% lignosulfonate showed no real difference from one day of storage contra two days. There was a high ratio of fines smaller than 1mm in size, approximately 50wt% of the total briquette weight was fines of this size, as can be seen from **Figure 27**.

6wt% lignosulfonate gave the drop test results given in **Figure 27**. The results from this batch shows that there is close to no difference between the two first days of storage. There is a lot of small fines being knocked loose form the agglomerate after two drops, and about 43% of the total weight is found as particles smaller than 1mm, and above 80% of the weight is passing through the 3.15mm screen. For this batch, there was a higher amount of fines captured on the 1mm screen than compared with the other two lignosulfonate batches. This is because the 2mm screen was not used in the sieve tower for the 6wt% lignosulfonate.

After two drops of the 8wt% lignosulfonate briquette batch, 40% of the total briquette batch was found as fines passing through the 1mm screen. The results from the first two storage days are given in **Figure 27**, and there is close to no significant change in strength between one and two days of storage. 80% of the briquette weight consists of fines passing through the 3.15mm screen.

From this analysis, the same is found as for compression test, that the briquette batch with the largest amount of binder produce the strongest briquettes.
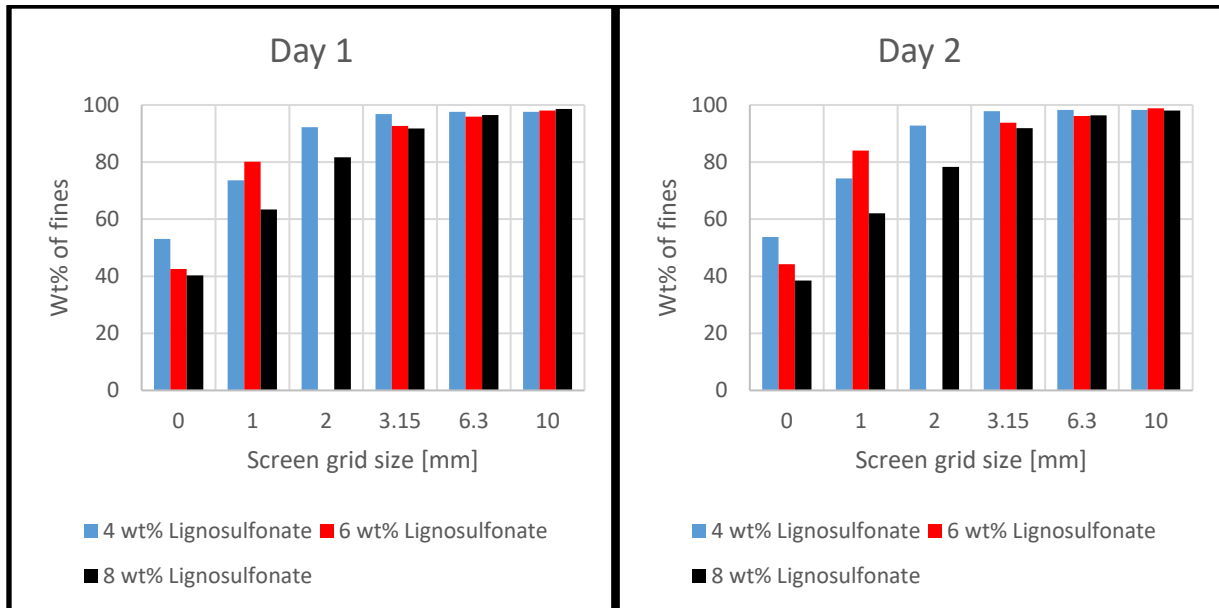
Figure 27: Screening analysis accumulated from the left from drop test of the 4, 6 and 8wt% lignosulfonate binder briquettes produced in the axial press. Left: One day of storage. Right: Two days of storage.

Bentonite: Shown in **Figure 28** are the results after one and two days of storage of the 1wt% bentonite binder briquettes. There is not much difference in number of fines created in the drop test after one and two days' storage. About 45% of the total briquette weight is found as fines passing the 1mm screen.
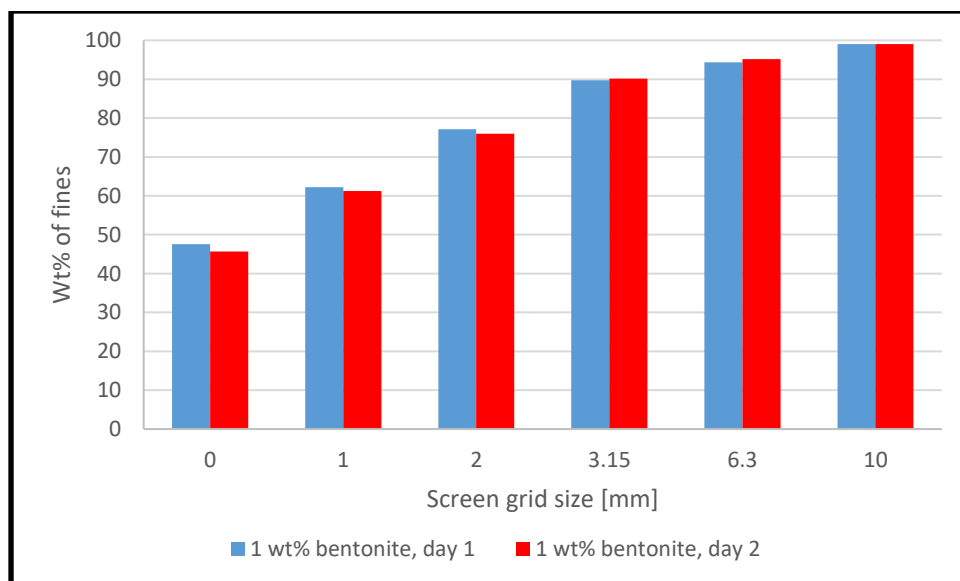
Figure 28: Screening analysis accumulated from the left from drop test of 1wt% bentonite binder briquettes produced in the axial press after one and two days of storage.

5.3.2. Roll-press Briquettes

Compression

Lime and molasses: The results of compression test for one and two days of storage of green briquettes with binder composition; 4wt% limestone and 8wt% molasses, are shown in **Figure 29**. It shows a slight decrease in strength from the first to the second day of storage, with compression strength of $118 \pm 12N$ and $101 \pm 12N$. The standard deviation is approximately the same for the two storage times.
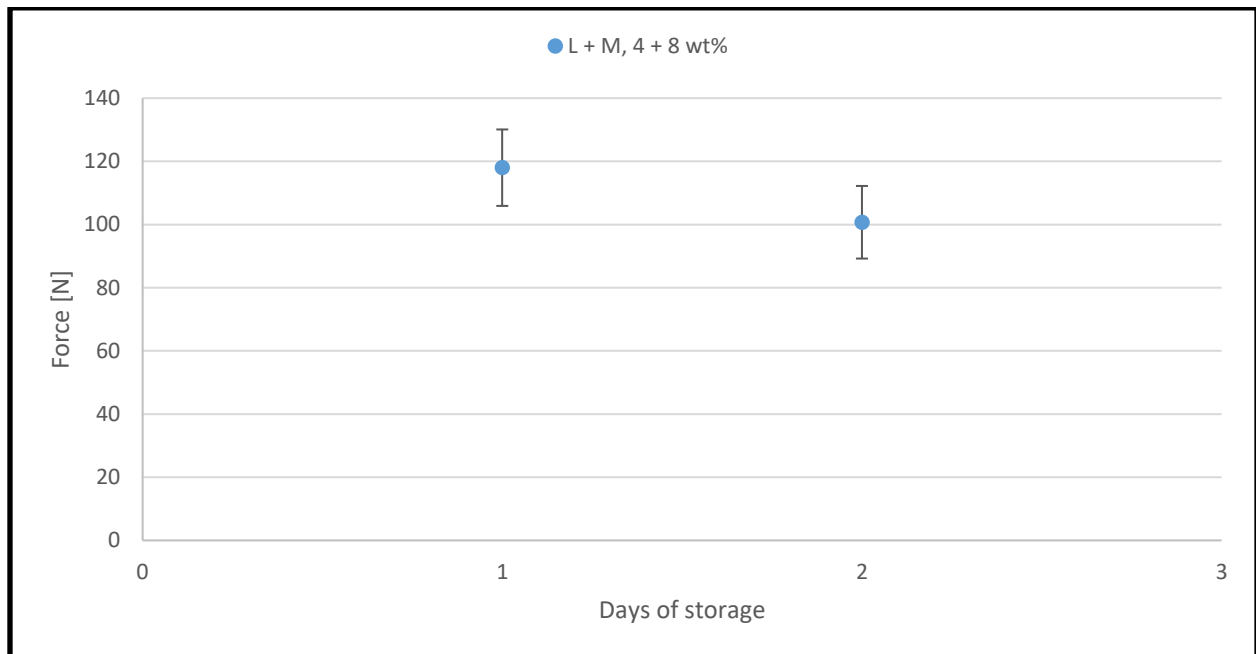
Figure 29: Compression strength of green lime 4wt% and molasses 8wt% briquettes after one and two days of storage.

Lignosulfonate: Compression results from the first two days of the 8wt% lignosulfonate is given in **Figure 30** and show good strength compared with the axial pressed briquettes with an average strength of $180 \pm 10N$ after one day of storage and $239 \pm 61N$ after two days of storage. The strength is rising from one to two days of storage, but the deviation is rising too.
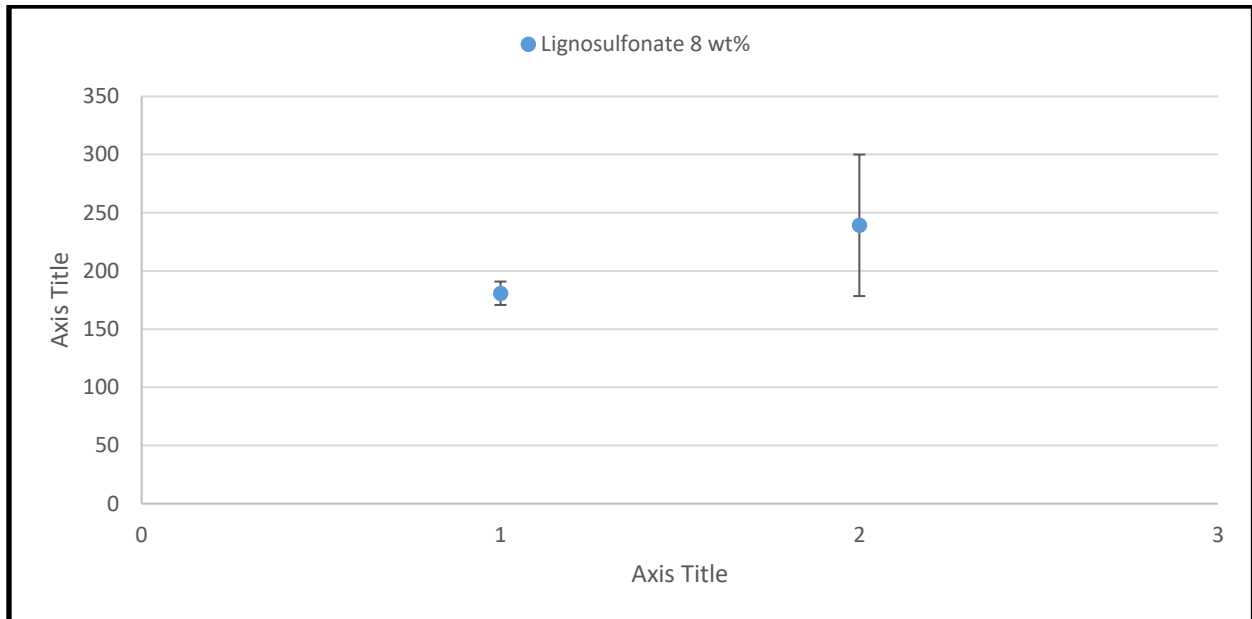
Figure 30: Compression test of 8wt% lignosulfonate produced the roll press after one and two days of storage.

Drop Strength

Lime and molasses: The drop test results for the 4wt% lime and 8wt% molasses briquettes are shown in **Figure 31**. There are only tiny amounts of particles breaking off from the green body after two drops, and 95-96wt% of the briquettes are found as particles larger than 6.3mm. There also seems to be only an indifferent difference in the results from one day of storage to two days.

The reason why the 6.3mm grid held such a large wt% after drop test was because the size of the briquettes after the wings (edges around the briquettes) broke off was small enough to fall through the 10mm screen. Out of the 40 briquettes drop tested of this binder composition, none was completely broken. Some cracks were observed, but the green body shape was still intact. What mainly broke off was the wings, these were very fragile. The wings are shown in **Figure 32**.

Results
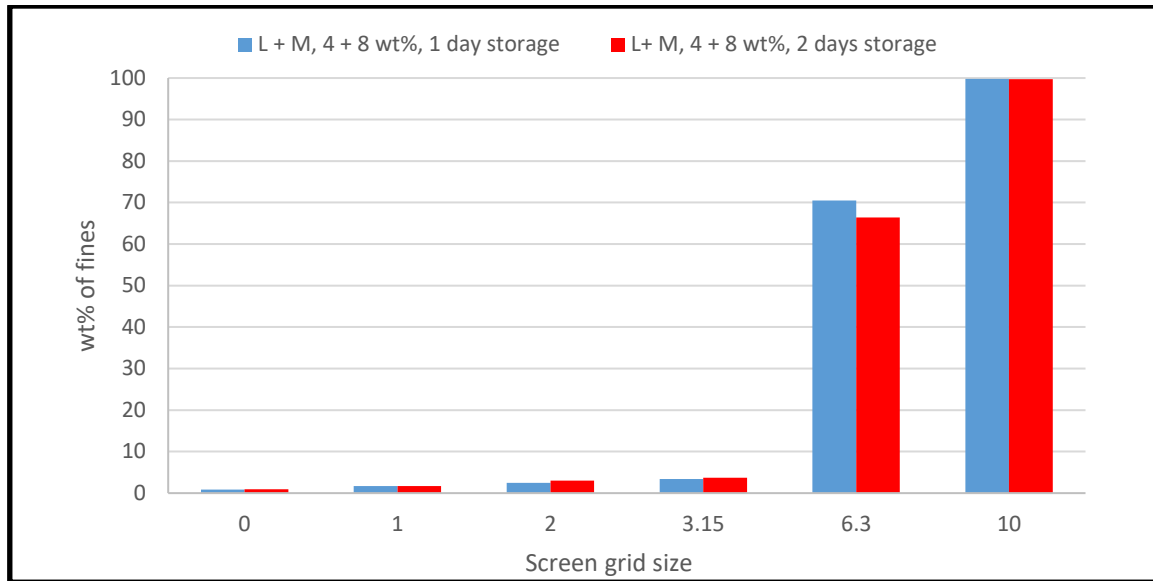
Figure 31: Drop test results of 4wt% limestone and 8wt% molasses binder briquettes for one day and 2 days of storage time. This graph gives the screen analysis after two drops from a height of 2m, and shows the sum of dust held at given screens accumulated to the right.
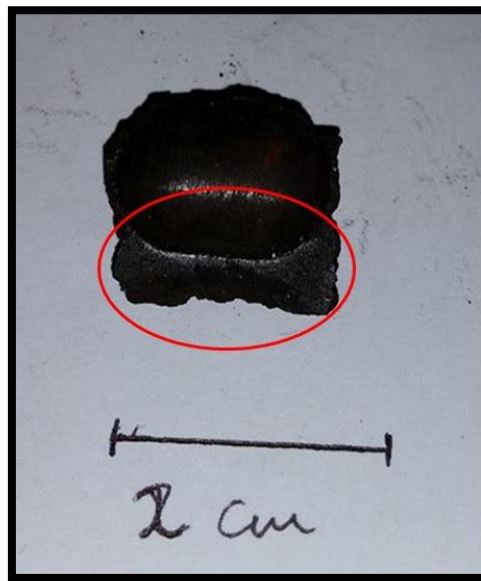
Figure 32: 8wt% lignosulfonate binder briquette. The edges on the side of the main body are referred to as wings (red circle).

Lignosulfonate: 8wt% lignosulfonate yielded the results shown in **Figure 33**. The results from one and two days of storage are plotted together, and there is no notable change in the strength from day one to two.

It can clearly be seen that these briquettes generate a lower amount of dust during drops than those made in the axial press. The wt% of fines smaller than 6.3mm in size is on average 5.16wt%, and compared with the axial press briquette of same composition with an average of 91.8wt% fines smaller than 6.3mm, implies briquetting method has a significant impact on strength.

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Results

As these briquettes had the same size as the lime and molasses briquettes, some whole briquettes fell through the 10mm screen. The same was observed with these briquettes as with the lime and molasses briquettes, namely that none broke after two drops. Some small cracks were observed, but the original shape was intact.
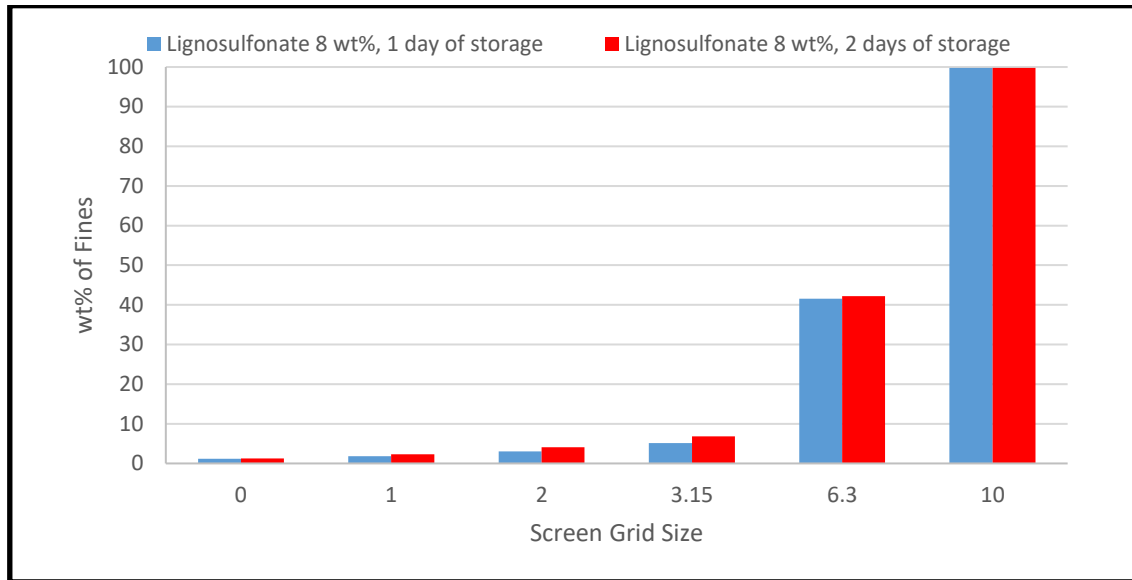
Figure 33: Drop test result of 8wt% lignosulfonate after one day of storage. This graph shows the amount in wt% of fines held at given screen grids after two 2m drops, accumulated to the right.

5.4. Long-term storage

The long-term storage batch of 3wt% lime and 6wt% molasses was not possible to test after one week of storage. When attempting to lift them out of the storage box, they crumbled to pieces. Instead the 4wt% and 8wt% roll pressed lime and molasses was stored and drop tested once more after 5 weeks. The results from this testing is given in **Figure 34** together with the results after two days of storage. As can be seen, there is no significant difference in the results from two days to 5 weeks.

In **Figure 35**, the weekly drop test results from the 6wt% lignosulfonate binder briquettes are shown. A slight increase of small sized fines is produced as the storage time increase, but the variation by storage time is small for the 5 weeks of storage for this batch. A deviation can be seen for the amount of fines collected on the 1mm screen for the samples stored for one and two days. This deviation is caused by not using the 2mm screen in the screening analysis for these two tests, leading to more fines being collected at the 1mm screen.

The same test performed on the 1wt% bentonite briquettes are shown in **Figure 36**. These briquettes steadily produced more fines for each storage week, but a deviation was found for week 2, were there was a significant increase in fines smaller than 1mm in the accumulated plot that did not fit with the steady increase form the other weekly tests.

44
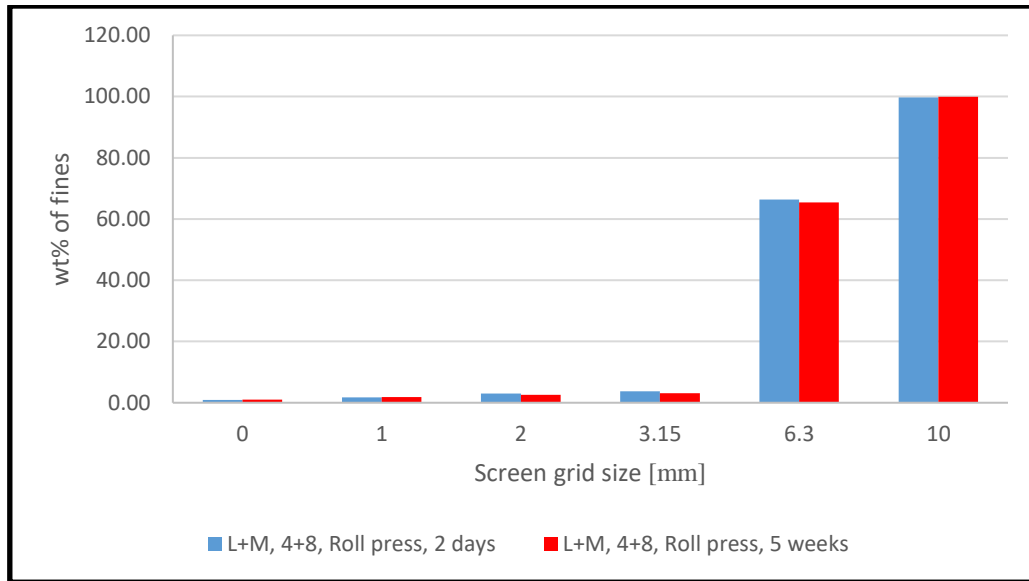
Results

Figure 34: Long-term storage drop test results from screen analysis of the 4 and 8wt% lime and molasses roll pressed briquette batch after storage for 2 days and 5 weeks.
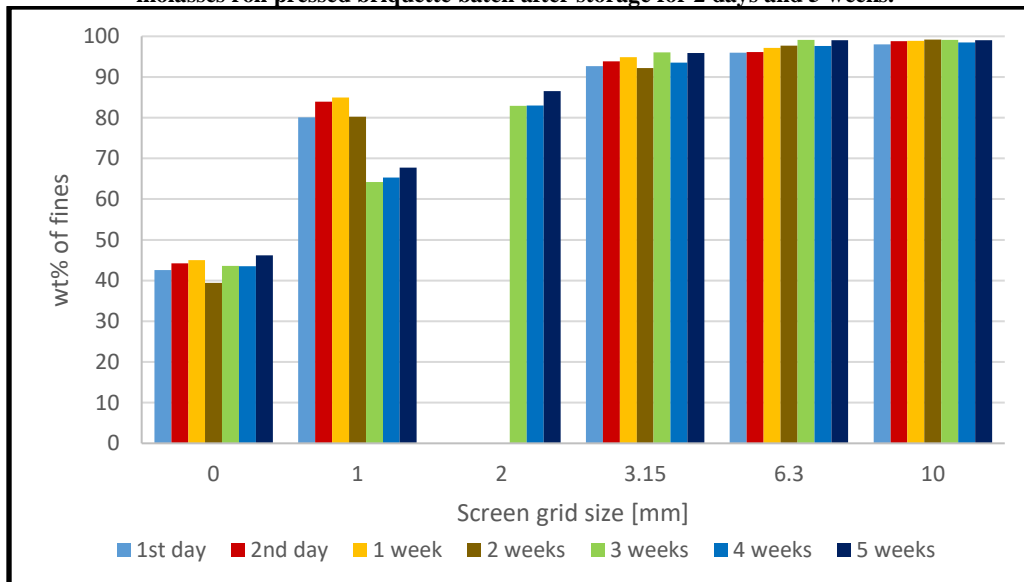
Figure 35: Long-term storage drop test, results from screening analysis of the 6wt% lignosulfonate briquette batch after storage for 1 and 2 days, 1, 2, 3, 4 and 5 weeks.
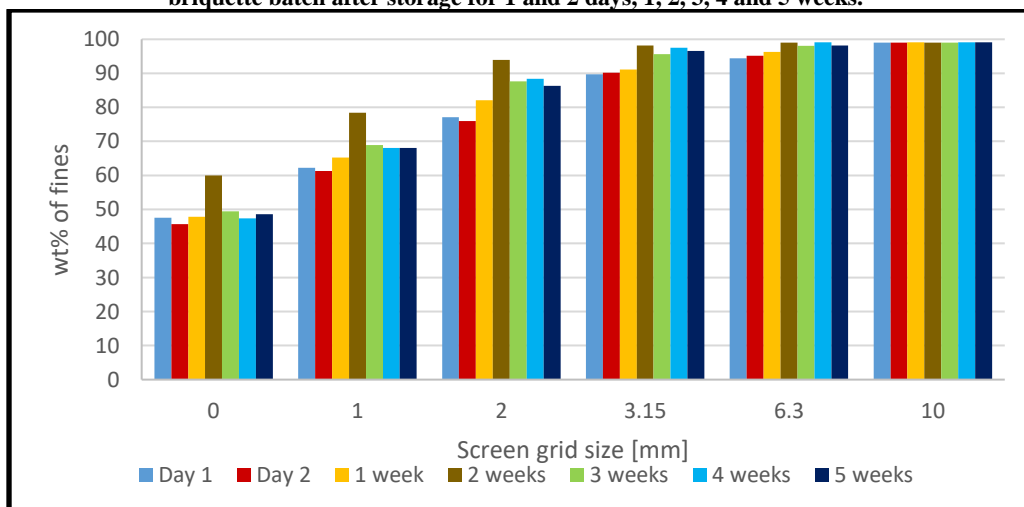
Figure 36: Long-term storage drop test results from screen analysis of the 1wt% bentonite briquette batch after storage for 1 and 2 days, 1, 2, 3, 4 and 5 weeks.

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5.5. Heat Treatment and Compression

As described in **Section 4.6**, the 8wt% lignosulfonate and 4 + 8wt% lime and molasses briquettes from roll-pressing were put through heat treatment at 105°C, 300°C, 500°C and 800°C. **Table 8** lists the visual observations from the heat treatments of these batches. The general trend was that as the temperature increased, more wings broke off from the main body and after 500°C, cracks started to form in the main bodies of both briquette batches. **Figure 37** depicts briquettes of both batches before and after heat treatment at 800°C. It is seen that the wings are almost completely gone for the briquettes that has been exposed to thermal treatment.

Table 8: Visual observations from heat treatment of the roll pressed batches; 4wt% lime/8wt% molasses and 8wt% lignosulfonate.

Temperature treatment	4wt% lime, 8wt% molasses	8wt% lignosulfonate
Green	Selected without any visible damage (cracks, misshaped) Glossy black color	Selected without any visible damage (cracks, misshaped) Glossy black color
105°C (drying)	No new defects were visible after drying	No new defects were visible after drying
300°C	No visible damage introduced to main body. Some of the wings started breaking off. Less glossy, but still black	No visible damage introduced to main body. Some of the wings started breaking off. Less glossy, but still black
500°C	More breakage of the wings. Some cracks visible at the surface of the main body. Browner than green state	More wing break-off Some cracks in main body, but less than the lime and molasses Browner than green state
800°C	Same as for 500°C, but some more cracking visible	Same as for 500°C, but some more cracking visible
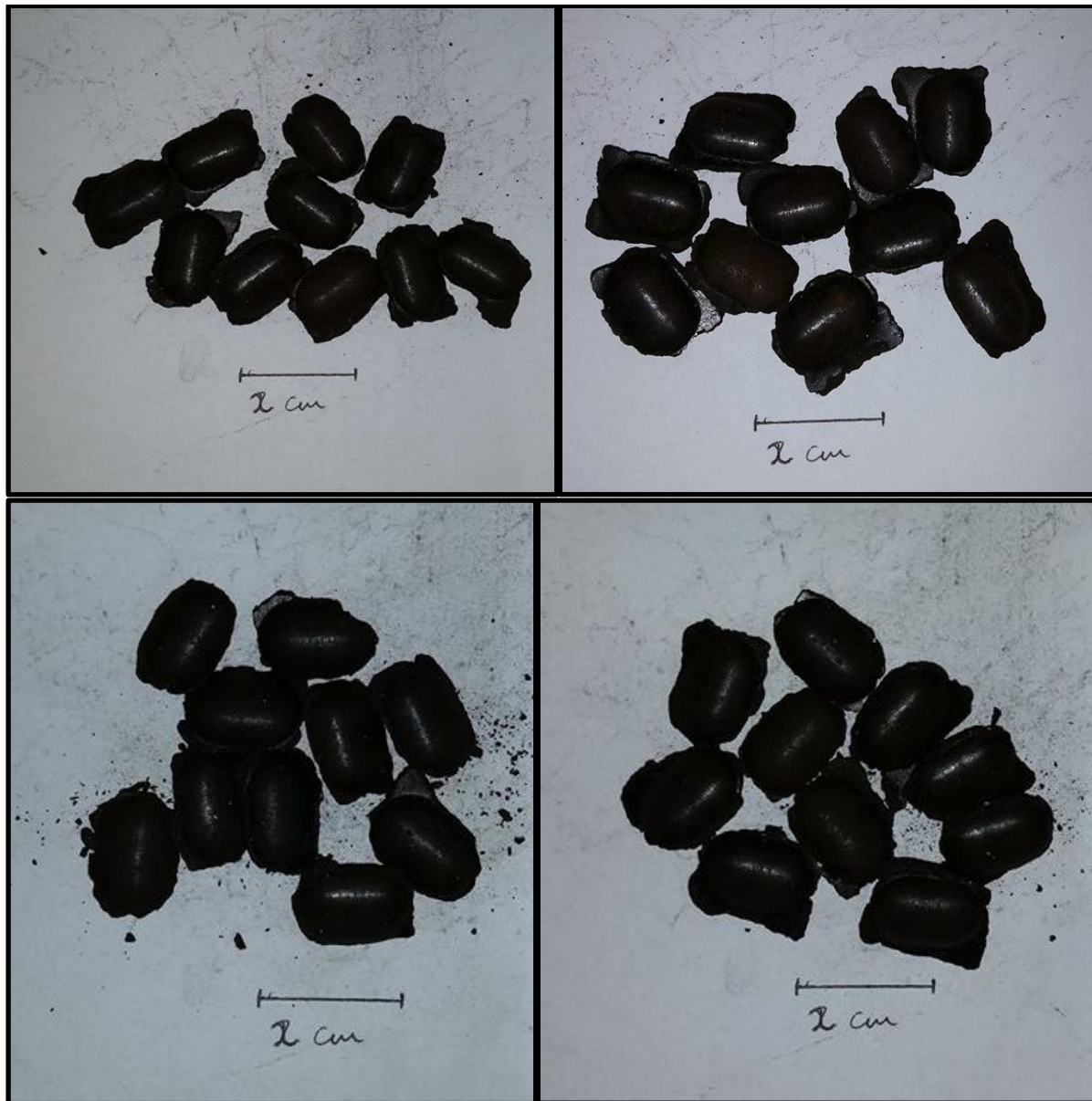
Figure 37: Top left: Briquettes with the 4wt% lime and 8wt% molasses binder before heat treatment. Top right: 8wt% lignosulfonate briquettes before heat treatment. Bottom left: 4wt% lime/8wt% molasses briquettes after heat treatment at 800°C. Bottom right: 8wt% lignosulfonate briquettes after heat treatment at 800°C.

Results

The results from compression test of the two roll press produced briquette batches are shown graphically in **Figure 38** and numerically in **Table 9**. The results also show a great increase in strength going from green briquettes to dry briquettes, then gradually decreasing strength with higher temperature. The 8wt% lignosulfonate has a higher strength during all stages, but after being heated to 500°C the lignosulfonate binder briquettes and the 4wt% lime and 8wt% molasses briquettes have approximately the same strength. From 500°C to 800°C, the strength is not changing noteworthy for either briquette type.

Table 9: Compression strength results of roll pressed briquettes before and after heat treatments [N].

Binder	1 day (Green) [N]	2 days (Green) [N]	Dry (105°C) [N]	Burnt 300°C [N]	Burnt 500°C [N]	Burnt 800°C [N]
8wt% lignosulfonate	181 ± 10	239 ± 61	415 ± 72	362 ± 59	162 ± 34	147 ± 24
4wt% lime, 8wt% molasses	118 ± 12	101 ± 11	346 ± 38	311 ± 43	137 ± 17	110 ± 17
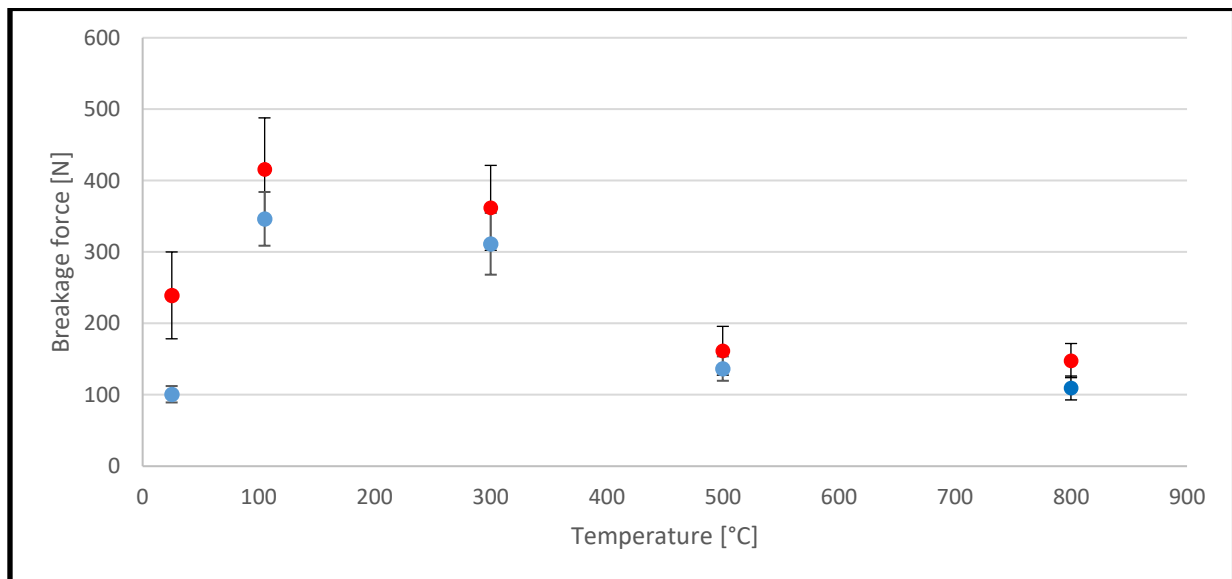
Figure 38: Compression strength of 8wt% lignosulfonate binder briquettes (red dots ●) and 4wt% lime and 8wt% molasses briquettes (blue dots ●) in green state and after heat treatment at 105°C, 300°C, 500°C and 800°C.

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5.6. Reference Ore

Results from strength tests of the reference ore is given in the following sections. In general, the reference ore is stronger and produce less dust than the green briquettes.

The compression test of the ore reference gave values of over 2000N. The test had to be aborted at this value due to apparatus limits, but all 5 lumps tested showed a compression strength of above 2000N.

As stated in **Section 4.6**, the ore reference was tested in the same manner as the briquettes. Results from drop test of the ore, **Figure 39**, shows that lumps larger than 10mm after two drops amount to 98wt% of total lump weight.
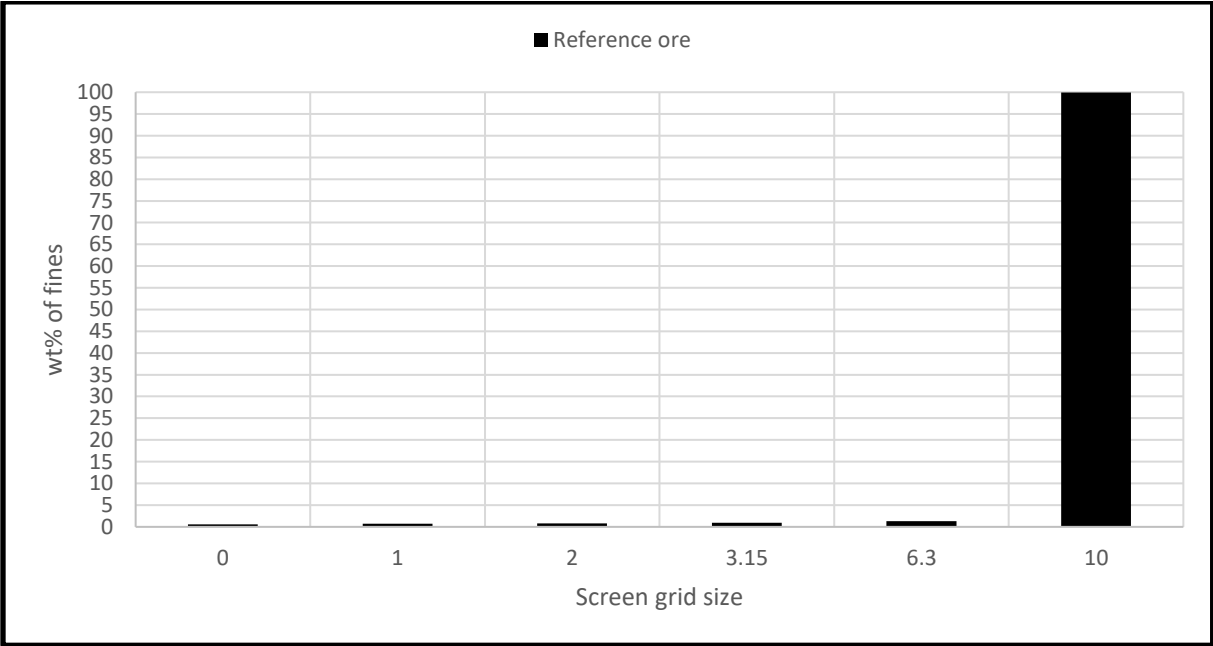
Figure 39: Results of drop test of ore lumps as a reference to the briquettes. This graph shows the amount in wt% of fines held at given screen grids accumulated from the left after two 2m drops.

6. Discussion

The main target of this study is to test binder materials potential to be used for cold-bonding of manganese oxide fines, producing agglomerates that will tolerate handling and transportation in green state and keep the agglomerates unbroken until the coke bed is reached during the production of ferromanganese alloys. For the agglomerates to be suited as furnace feed, some demands must be met and the following sections will look at the results from testing up against each other and reflect on the suitability towards being used as charge material.

First up, the sightings from mixing and binder properties will be discussed, then the relative strength of axial press briquettes and roll press briquettes. The method of briquetting will take up the next section, then storage and a reflection of potential usability will be the last section ending the discussion.

6.1. Mixing and Binder Materials

The axial press technique of agglomeration was not believed to produce desirably strong and dense briquettes, but rather to give consistent and directly comparable results between the different binders and dosages. The method in general was straight forward, the main reason for uncertainty came from the mixing process, which is quite difficult to decide if is similar from batch to batch.

The idea of the binder is to create a bridging structure between the fines, adsorbing on the surface of the fines and bonding them through the binder (**Section 3.3**). For this to be possible, the binder must spread and be distributed. Observations and qualities of the binders used are summarized in **Table 6** in **Section 5.1**.

As presented in the experimental chapter, three different binder types were tested in this project. The workability of the binders was quite different from each other. The simplest binder of the three to use and distribute into the mix was the bentonite powder, as it was dry and not too cohesive and had a contrasting color to the fines, which made it possible to see when there were no large local concentrations of the binder. It did seem to distribute well among the dry fines. The same is seen from the strength results from drop and compression tests, as they were stronger than the 4wt% lignosulfonate and very closely matched with the 6wt% lignosulfonate.

The lignosulfonate binder was easy to handle too, due to its low viscosity. It was easy to portion out and not too adhering to smooth surfaces. In mixing it distributed fast and spread well throughout the dry fines. A distinct color change made it clear that it was well mixed. The color change was not as distinct for the 4wt% lignosulfonate as for the two higher dosages. This is believed to be one of the reasons why the 4wt% dosage produced weaker briquettes, the amount of binder was too low to completely wet all the fines and not creating a bridge network between all the fines.

The lime and molasses on the other hand was sticky and adhering to all surfaces, had high viscosity and hard to portion in the right amount. If the mixing speed was too low when adding this binder, large pools of binder collected and was not distributed to the raw material fines. It did not seem to be spreading well and needed high rotating speed to be distributed preferably.

On another note, the lime and molasses did collect a lot of fines due to its sticky nature, but this might as well be the reason why the two lowest amounts of this binder did not produce stronger briquettes with the axial press method. Rather than spreading between the particles and

bonding them to each other, the lime-molasses seemed to collect particles in small, pellet-like agglomerates, leading to no real connection between those pellets when pressed in the axial press. This problem did not occur when the dosage of lime and molasses was raised to 4 and 8wt% respectively, then the binder spread easier through the raw material fines, the small pellets were not formed and the mix attained a more uniform darker color.

For the lime and molasses, longer mixing time is necessary to obtain an acceptable mixture, due to the high viscosity of the binder. From **Section 3.3** the relationship of viscosity and spreading is described and how the increased viscosity retards the spreading of binder through a powder bed. This was highly visible from these experiments as well, as it was crucial for the addition of this binder that the mixer was running at high speed to be able to distribute the binder.

One option for the lime and molasses binder is to heat it slightly before addition to lower the viscosity, which in turn will make the binder addition step and mixing faster.

6.2. Briquette Strength

Lignosulfonate: The drop test results from the lignosulfonate briquettes after one and two days of storage were shown in **Figure 27** in **Section 5.3**. As the figure shows, there was little to no difference after curing from one to two days and the amount of fines created after two drops is lower as the binder dosage is increased. As discussed in the previous section this seems to cohere with the observations from mixing.

There is one significant point that stand out considering that increased binder concentration gives less fines, namely the dust collected on the 1mm screen from the 6wt% lignosulfonate briquettes. The reason why there is more dust at this screen for the 6wt% vs. the 4wt% is because that for the 6wt% screening, the 2mm screen was not used in the sieve tower, leading to this fraction also being stopped and held at the 1mm screen. For the rest of the measurements, the 6wt% lignosulfonate is between the 4wt% and 8wt% in dust freed from the green body after drop impact.

The compression test also shows the same result as the drop test. 6wt% lignosulfonate briquettes gave results between the 4wt% and 8wt% lignosulfonate briquettes, the 8wt% being the strongest and 4wt% the weakest. This cohere well with the theory posted in **Section 3.3**, that a higher amount of binder will result in more nucleation points for agglomeration and a higher degree of wetting of particles, creating a stronger bonded agglomerate [13].

Lime and molasses: The compared results from the lime and molasses briquettes after drop test are shown in **Figure 25**. The results after one day of storage is in the graph to the left and after two days to the right. For these briquettes, there was an enormous difference between the two dosages. The 3wt% of limestone and 6wt% of molasses was creating a lot of dust during handling while the 4wt% limestone and 8wt% molasses was creating much less overall. It should be mentioned that, as described in the Axial Press-**Section 5.2**, the 2wt% limestone and 4wt% molasses did not make the short transport from the production to the storage room either.

There is the possibility that the two smallest amounts of lime and molasses tested in this work were not completely homogeneously mixed, as the difference in results from the 3 and 6wt%, and 4 and 8wt% lime and molasses was that large and the 2wt% and 4wt% lime and molasses did not complete transport.

<u>Discussion</u>

From other research, it has been found that the lime and molasses binder has a peak in strength after approximately 48 hours of storage [46], this is partly found from these experiments, but it only seems to fit for the 4wt% lime and 8wt% molasses batch. The amount of dust released from drop of the 4 and 8wt% lime and molasses shows a clear improvement from 24 hours to 48 hours of storage. The compression strength improves as well (**Section 5.3**, **Table 7**), implying the curing reaction, **Section 3.3.2**, occurs for the 4 and 8wt% lime and molasses axial pressed batch, but not for the 3 and 6wt%. The main reason for this is not believed to be the reaction itself, but rather the mixing of the binder and fines.

This binder type was also the only binder showing briquettes close to the strength of the reference ore, even though the agglomeration method was not predicted to give strong briquettes, due to the height-to-width ratio of the axial pressed briquettes (**Section 3.5**).

From **Figure 40** one can see the drop test results from the strongest lignosulfonate binder briquette batch and the strongest lime and molasses briquette batch compared with the drop test results from the reference ore. The ore is much stronger than the strongest of the axial pressed briquettes.
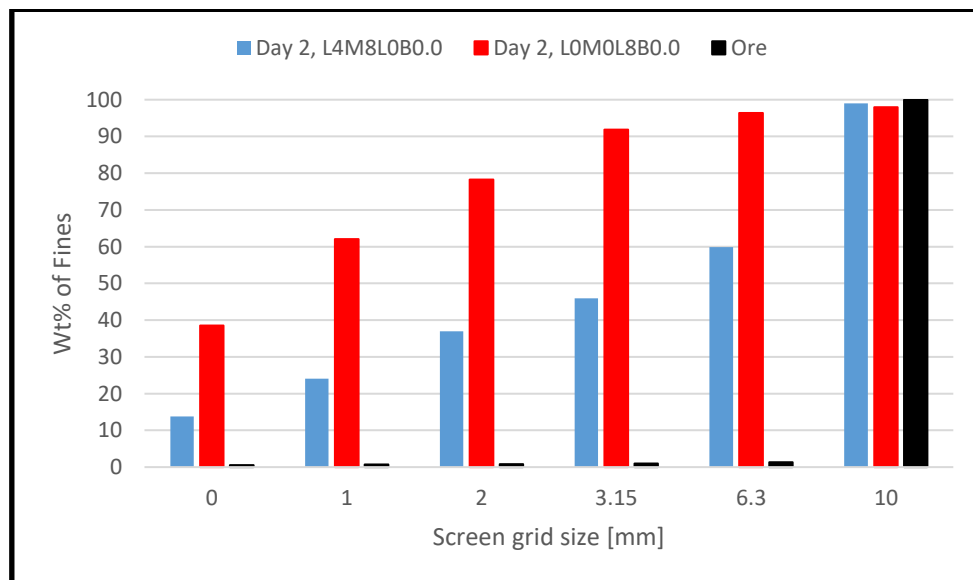
Figure 40: Accumulated screen analysis of the strongest briquettes from axial press briquetting after drop test compared with the reference ore.

Bentonite: The 1wt% bentonite batch showed promising results, it produced less fines from drop test than the 4 and 6wt% lignosulfonate batches and a change in strength was not visible from one day of storage to two (**Figure 41**). Due to the high amount of impurities introduced to a furnace by use of bentonite as a binder, it was tested in a low amount. As the results shows, this binder dosage of bentonite was not close enough to the high dosage organic binders. A higher dosage of bentonite is believed to produce stronger briquettes, as it will connect more particles, but the impurities it supplies to the furnace is a strong drawback.
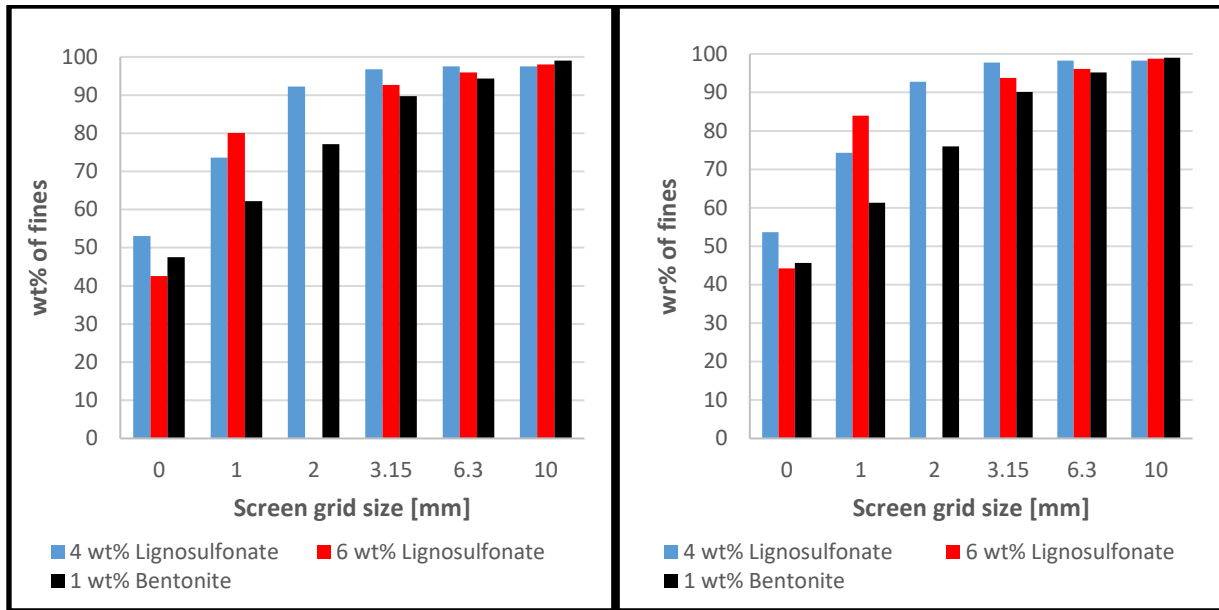
Figure 41: 1wt% bentonite, 4wt% lignosulfonate and 6wt% lignosulfonate. Left: after one day storage, Right: after two days of storage

6.3. Briquetting Method

As presented in **Section 5.3**, the roll pressed briquettes gave a higher strength than the axial pressed briquettes. In **Figure 42**, the results from the 8wt% lignosulfonate and 4 and 8wt% lime and molasses drop tests of both the axial pressed and roll pressed batches are presented. The binder showing the largest change in test results with change of briquetting method is the lignosulfonate briquette. From drop test, the lime and molasses binder briquettes were the strongest and the same is visible for both the roll press and axial press batches, though the difference between the two binders is smaller for the roll pressed briquettes. From **Figure 42** it shows that the axial pressed briquette of lime and molasses has a lower wt% of material collected at the 6.3mm screen than the roll pressed, but this is misleading, as the roll pressed briquettes' size was small enough to fall through the 10mm screen, while they in fact did not actually break from the drops (**Section 5.3**).

The main reason for the big gap in strength between the briquetting methods is believed to be caused by the pressure distribution difference of the two production methods. The roll pressed briquettes has a much lower height-to-width ratio than the axial pressed ones, which gives a more uniform density throughout the agglomerate. In addition, the compaction pressure of the roll press was almost 3 times that of the axial press, contributing further to the compaction of the fines and the strength of the agglomerates. Another benefit of the roll press contra the axial press is the lack of side walls in the die, eliminating the wall-particle friction which may lead to less compact agglomerates (**Section 3.5**).

In terms of compression strength, the lime and molasses briquettes made from axial press and roll press did not differ by a large margin, and after curing at room temperature for two days they displayed approximately the same strength (see **Figure 43**). The strengthening effect seen by this binder briquette from the axial press was not reflected in the roll pressed batch. The lignosulfonate briquette, on the other hand, had a significant increase in compression

<u>Discussion</u>

strength when produced with the roll press contra axial press. This increase in strength was expected to be found for both binders, but that was not the case.

As both roll pressed binder briquettes displayed stronger results in drop test, only the lignosulfonate binder showed a significant increase in compression strength. It is believed that the roll press method has an overall increasing effect on strength for the briquettes. The reason of no change in compression strength results of the lime and molasses binder must be due to the binder itself, not the briquetting method. The low compression strength after two storage days might be due to incomplete curing reaction, as the strength after one day of storage is much greater than for the same composition axial pressed briquette.

In addition to changing briquetting method, the metallic fines were excluded from the roll press recipe. This makes it unclear how much of the change in strength test results arise from briquetting method or recipe change. Some gained strength may result from lack of voids forming around hard metallic particles, **Section 3.5.1**.
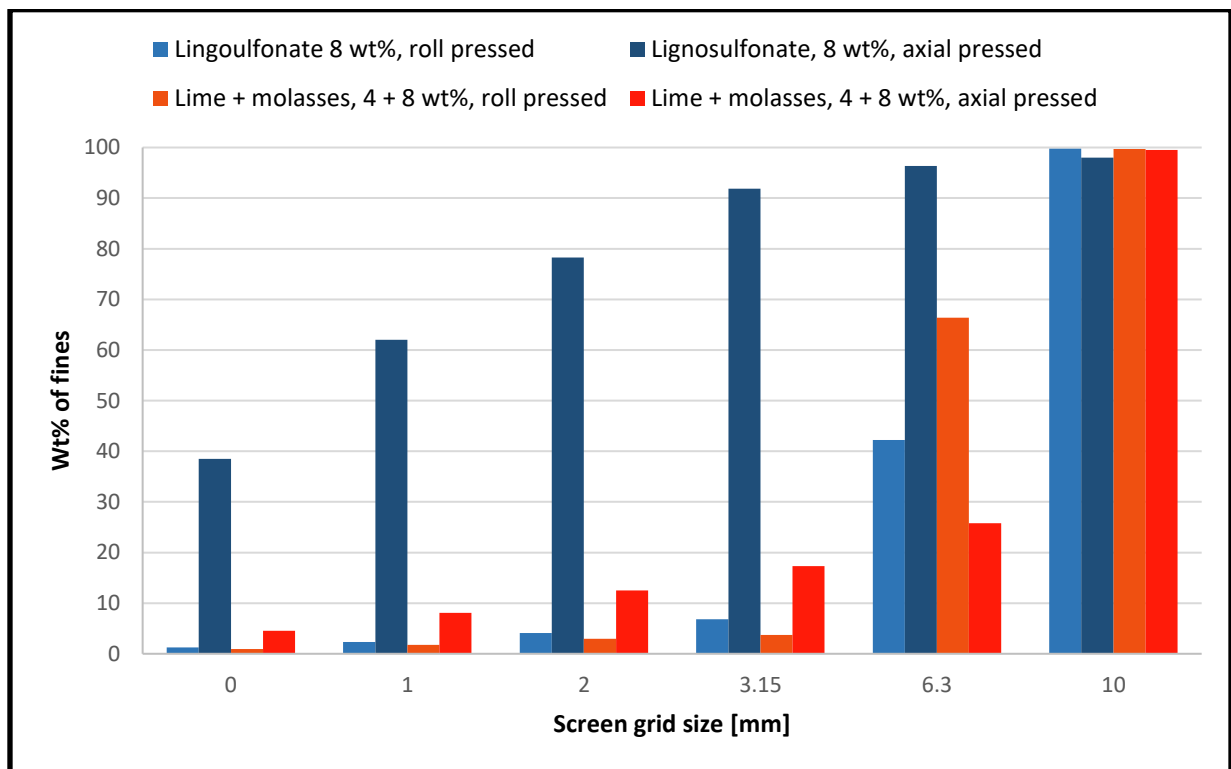
Figure 42: Comparison of the drop test screening analysis (accumulated) of the roll pressed and axial pressed briquettes of 8wt% lignosulfonate and 4 + 8wt% lime and molasses after two days of storage.
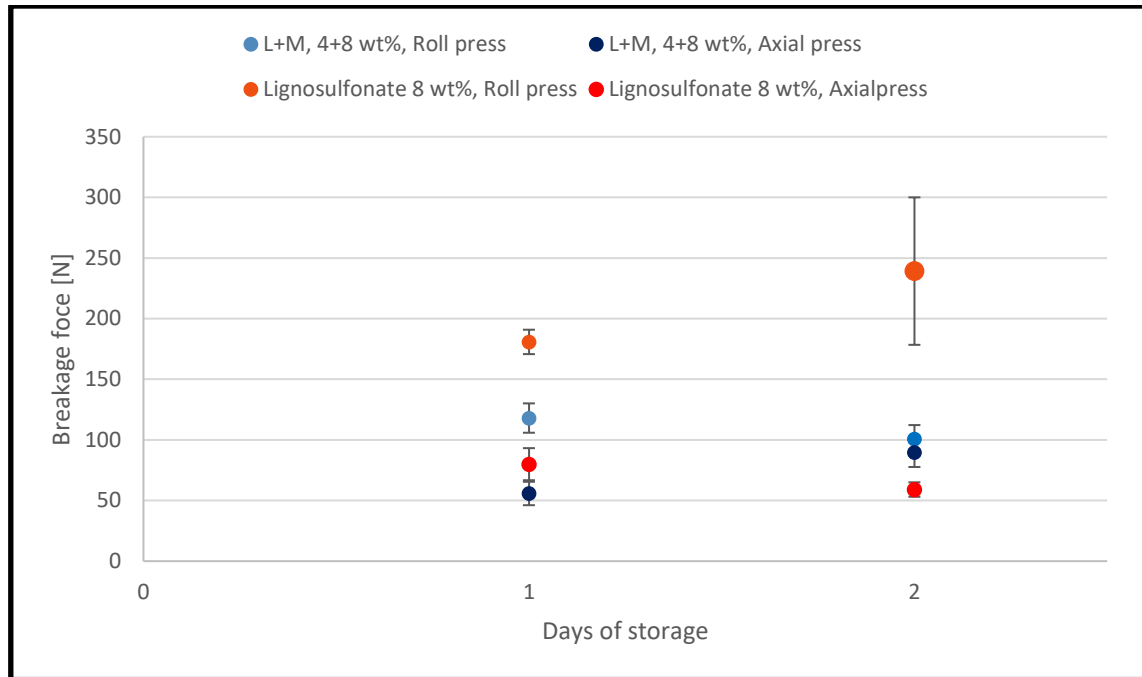
Figure 43: Comparison of compression strength of 8wt% lignosulfonate, and 4wt% lime and 8wt% molasses, both axial pressed and roll pressed briquette batches.

6.4. Storage

One thing that was found by coincidence from the pre-study for this thesis was that the organic binder briquettes made from lime and molasses were degrading heavily during long time storage [34]. This was attempted reproduced and monitored during this research by testing the drop strength of them once per week after production. Unfortunately, the lime and molasses batch made for the long-term storage did not hold, so consistent results from this batch was not possible to observe. This was instead tested by the leftover briquettes from the roll press production of lime and molasses briquettes. Due to the small number of briquettes left, only one long term storage drop test for this batch was done, after a storage time of 5 weeks.

Figure 44 underneath has the results from drop test against storage time of the 6wt% lignosulfonate and the 1wt% bentonite briquettes made with the axial press. For this comparison, the accumulated fines smaller than 6.3mm are shown. As for all the axial pressed briquettes, the quantity of fines produced during drop test was high, but there seems to be no sign of degrading from the results gathered of these two batches, if any, it is the bentonite batch that has the most stable decrease in strength with increased storage time, which is at 6wt% higher after 5 weeks contra 1 day.

The bentonite briquettes also had a low standard deviation compared with the 6wt% lignosulfonate briquettes, which suggests that the bentonite briquettes are more stable and more homogeneously mixed, producing more evenly and predictably performing agglomerates.

The 4wt% lime and 8wt% molasses batch from the roll press did not change any in drop strength after 5 storage weeks (**Figure 34**). This imply that storage environment is an important criterion to degradation by storage time. From this work, briquettes were stored under dry conditions at an average temperature of 21°C.

<u>Discussion</u>
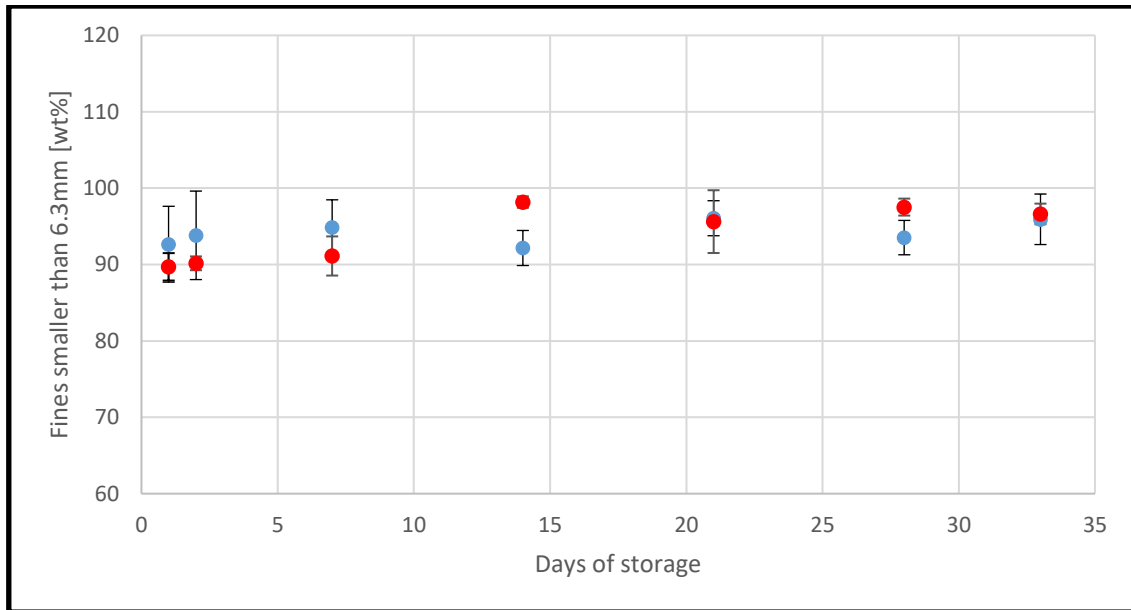
Figure 44: Plot of the amount of fines smaller than 6.3mm produced after drop test as a function of storage days of the 6wt% lignosulfonate binder (blue dots •) and the 1wt% bentonite binder (red dots •) briquettes.

The most prominent change found in the previous study was that a green/blue mold formed on the briquettes, but this was not found in this work, where some of the briquettes had been stored for up to 2 months. The reason for the lack of mold on the briquettes produced for this thesis might be because these briquettes were stored unsealed and in contact with air with low humidity, while the pre-study briquettes were stored in sealed and air tight boxes with a high degree of humidity. As described in **Section 3.3.2**, humidity is one of the most crucial factor for mold growth, together with nutrition. Molasses is a form of sugar, which is nutritious and will give fungi what is needed to grow.

Storing the briquettes in a dry environment might not be enough to avoid mold growth, as the briquettes are wet in green state, but from the results from this work it seems that storage in a dry environment reduce the chance of this mold. As also stated in **Section 3.3.2**: *The surface must exceed a 30-day running average of 85% humidity for mold growth to be visible [35]*. If the storage time of the briquettes is kept to less than 30 days before use, this should not be a problem.

6.5. Furnace Performance

In **Figure 45** the drop test results of the roll pressed briquettes are compared with the reference ore. The produced fines from the drops of roll pressed briquettes are low, but they are still not as good as the ore. The lignosulfonate binder briquettes produced over 5wt% fines smaller than 6.3mm on average after two drops of 2m, while the ore has only produced 1wt%. The lime and molasses is still under 4wt%, but they are not as strong as the ore. Both briquette batches however is below the 15% limit of fines smaller than 6mm fed to a closed furnace by a good margin in green state(**Section 3.1**[11]).

<u>Discussion</u>
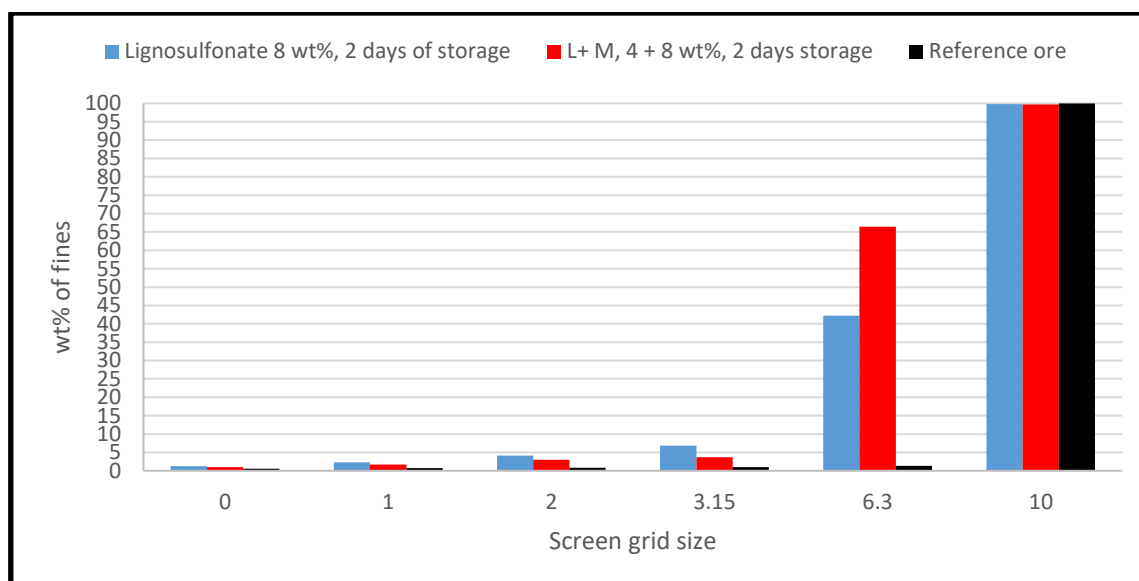
Figure 45: Comparison of drop test screening analysis (accumulated from left) of the roll pressed briquettes and the reference ore.

In the pre-reduction zone of the manganese production furnace the charge material is descending while heated by ascending gas. The pressure from surrounding charge material will increase on downward, and the compression strength of the constituents of the charge is important. In green state, the briquettes are far weaker than the reference ore. From **Section 5.3** and **Figure 38** it is shown that the roll pressed briquettes has about 10% of the compression strength of the ore, and when they arrive at 800°C the briquettes have not gained any strength from sintering. As the briquettes are much weaker than the ore material, this leads to them breaking before the ore if the pressure is too high.

One positive aspect of the briquettes compression strength is that they do not drop much in strength after binder burn-off compared with green state. This way it will be expected that they will not decline much in performance descending in the furnace. Another prediction will be that as the binder burns off, it will leave additional pores in the briquettes[33], lowering the strength [16], but increasing the reactivity.

Cracking will also be a risk when the binder is gone, as a sudden increase of pore volume also may induce cracks in the agglomerate (**Section 3.3.2.1**). From visual inspection of the briquettes after heating, more cracks were seen after the 800°C treatment. This suggests a further decrease in strength as the process proceeds, this until sintering starts to densify and strengthen the briquettes.

Overall, the behavior of these roll pressed briquettes with an organic binder show the same results as seen from M. Sunde's work on ilmenite pellets[14], but these briquettes needs higher temperatures than the ilmenite briquettes to strengthen from sintering. This due to the high temperatures needed to induce sintering in manganese oxide (1200°C).

7. Conclusion

Mixing: The mixing procedure of different fines is best performed when the sludges are dried before addition, to avoid small pellets being created. Of the binders used, lignosulfonate was the easiest to prepare and the best flowing and wetting of the two liquid binders. Dried bentonite fines were the simplest binder to use overall. Lime and molasses was the most challenging binder when mixing and was the slowest to distribute fairly.

- Binders in decreasing order of workability: Bentonite, lignosulfonate, lime/molasses

Strength of Binder: 8wt% lignosulfonate produced the strongest briquettes in terms of compression strength, while the 4wt% lime and 8wt% molasses binder gave the best results from drop impact test and binder dosage is crucial to briquette strength.

- 8wt% lignosulfonate strongest in compression
- 4wt% lime, 8wt% molasses strongest in drop strength
- Higher dosage of binder = stronger briquettes

Briquetting Method: Of the two briquetting methods used, uniaxial pressing and roll pressing, roll pressing created the strongest briquettes. This is believed to be caused by the lack of side-wall friction and low height-to-width ratio of the roll press.

Storage: If either the storage facility is kept dry or the briquettes are stored for less than 30 days, mold growth is not believed to be a problem.

Furnace Potential: The fines/dust produced from drops of 2m of green briquettes made with 4wt% lime and molasses, and 8wt% lignosulfonate is below the proposed safety limit of 15% for a closed SAF. From 300°C and to at least to 800°C, the strength will drop in the briquettes and there is the risk of cracking due to burn-off of the organic binder. It is not possible to conclude how well they will tolerate the safety limit during descending with the charge in the industrial process from this work, but both lime and molasses, and lignosulfonate briquettes are promising.

- Both organic binders produce satisfactory green strength briquettes
- Both organic binders are weakening from 300°C and up to 800°C

8. Further Work

Further work is needed on briquetting of waste dust from the ferroalloy production. This includes investigation of the CO-reactivity of these agglomerates, pore volume analysis and make use of the work of J. R. Johanson [44] to optimize briquetting parameters for this fines mixture.

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Appendix

A1: Raw Data from Drop Test

Table 10: Screen analysis of 4wt% lignosulfonate after drop test

1st day	W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<2mm	<1mm	sum a/screen
1	23.15	22.62	0.00	0.00	1.37	4.16	4.80	12.18	22.51
wt%			0.00	0.00	5.92	17.97	20.73	52.61	97.24
2	22.92	22.43	0.00	0.00	1.42	3.97	4.96	11.99	22.34
wt%			0.00	0.00	6.20	17.32	21.64	52.31	97.47
3	23.81	23.49	0.00	0.73	0.51	4.70	4.96	12.48	23.38
wt%			0.00	3.07	2.14	19.74	20.83	52.41	98.19
4	23.81	23.36	0.00	0.00	0.97	4.61	4.55	13.04	23.17
wt%			0.00	0.00	4.07	19.36	19.11	54.77	97.31
Avg.wt%			0.00	0.77	4.58	18.60	20.58	53.03	97.55

2nd day	W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<2mm	<1mm	sum a/screen
1	22.96	22.63	0.00	0.00	1.09	4.73	4.78	11.92	22.52
wt%			0.00	0.00	4.75	20.60	20.82	51.92	98.08
2	24.64	24.41	0.00	0.00	1.29	5.06	5.19	12.82	24.36
wt%			0.00	0.00	5.24	20.54	21.06	52.03	98.86
3	21.29	20.82	0.00	0.40	0.86	3.24	4.77	11.46	20.73
wt%			0.00	1.88	4.04	15.22	22.40	53.83	97.37
4	21.69	21.49	0.00	0.00	1.34	3.80	3.93	12.36	21.43
wt%			0.00	0.00	6.18	17.52	18.12	56.98	98.80
Avg.wt%			0.00	0.47	5.05	18.47	20.60	53.69	98.28

A1: Raw Data from Drop Test

Table 11: Screening analysis of 6wt% lignosulfonate axial press

Day 1		W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<1mm	sum a/screen
	1	40.18	39.48	0.00	2.03	4.67	15.73	16.87	39.30
wt%				0.00	5.05	11.62	39.15	41.99	97.81
	2	37.13	36.73	0.00	0.00	5.17	14.01	16.86	36.04
wt%				0.00	0.00	13.92	37.73	45.41	97.06
	3	37.41	37.56	0.00	1.24	4.76	14.18	16.64	36.82
wt%				0.00	3.31	12.72	37.90	44.48	98.42
	4	37.89	37.56	3.13	1.84	4.56	13.38	14.53	37.44
wt%				8.26	4.86	12.03	35.31	38.35	98.81
Avg.				2.07	3.31	12.58	37.52	42.56	98.03
Day 2		W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<1mm	sum a/screen
	1	36.64	36.42	0.00	1.30	2.95	14.62	17.29	36.16
wt%				0.00	3.55	8.05	39.90	47.19	98.69
	2	35.92	35.71	0.00	0.00	3.93	15.44	16.24	35.61
wt%				0.00	0.00	10.94	42.98	45.21	99.14
	3	39.01	38.75	4.13	1.03	4.31	14.02	15.05	38.54
wt%				10.59	2.64	11.05	35.94	38.58	98.80
	4	37.04	36.66	0.00	1.13	3.47	14.85	17.03	36.48
wt%				0.00	3.05	9.37	40.09	45.98	98.49
Avg.				2.65	2.31	9.85	39.73	44.24	98.78
1 Week		W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<1mm	sum a/screen
1		35.62	35.32	2.43	0.51	3.58	15.56	13.21	35.29
wt%				6.82	1.43	10.05	43.68	37.09	99.07
2		34.24	34.01	0.00	0.00	3.08	14.12	16.68	33.88
wt%				0.00	0.00	9.00	41.24	48.71	98.95
3		34.18	33.82	0.00	1.94	2.25	13.20	16.35	33.74
wt%				0.00	5.68	6.58	38.62	47.83	98.71
4		36.18	35.84	0.00	0.79	4.99	13.22	16.73	35.73
wt%				0.00	2.18	13.79	36.54	46.24	98.76
Avg.				1.71	2.32	9.86	40.02	44.97	98.87
2 weeks		W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<1mm	sum a/screen
1		35.00	34.77	0.00	3.73	4.64	14.39	12.03	34.79
wt%				0.00	10.66	13.26	41.11	34.37	99.40
2		34.44	34.05	0.00	1.85	4.40	14.00	13.84	34.09
wt%				0.00	5.37	12.78	40.65	40.19	98.98
3		36.01	35.75	2.18	0.00	4.18	14.17	15.13	35.66
wt%				6.05	0.00	11.61	39.35	42.02	99.03
4		35.75	35.49	0.00	2.18	3.56	15.08	14.72	35.54
wt%				0.00	6.10	9.96	42.18	41.17	99.41
Avg.				1.51	5.53	11.90	40.82	39.44	99.21

A1: Raw Data from Drop Test

3 weeks	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	36.04	35.73	0.00	1.68	4.62	6.26	7.41	15.75	35.72
wt%			0.00	4.66	12.82	17.37	20.56	43.70	99.11
2	35.24	34.86	0.00	1.01	4.15	7.35	7.53	14.78	34.82
wt%			0.00	2.87	11.78	20.86	21.37	41.94	98.81
3	35.72		0.00	1.19	4.23	7.13	7.69	15.16	35.40
wt%			0.00	3.33	11.84	19.96	21.53	42.44	99.10
4	35.64	35.34	0.00	0.52	5.70	6.03	7.69	15.53	35.47
wt%			0.00	1.46	15.99	16.92	21.58	43.57	99.52
Avg.			0.00	3.08	13.11	18.78	21.26	42.91	99.14

4 weeks	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	35.01	34.68	1.20	1.84	3.75	5.79	7.26	14.92	34.76
wt%			3.43	5.26	10.71	16.54	20.74	42.62	99.29
2	33.73	33.36	0.00	1.93	3.07	5.47	7.84	15.07	33.38
wt%			0.00	5.72	9.10	16.22	23.24	44.68	98.96
3	33.14	32.34	0.00	1.03	3.10	6.40	6.92	14.82	32.27
wt%			0.00	3.11	9.35	19.31	20.88	44.72	97.37
4	34.09	33.54	0.00	0.77	4.44	6.30	7.60	14.38	33.49
wt%			0.00	2.26	13.02	18.48	22.29	42.18	98.24
Avg.			0.86	4.09	10.55	17.64	21.79	43.55	98.47

5 weeks	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	33.97	33.65	0.00	0.00	3.46	7.00	7.34	15.79	33.59
wt%			0.00	0.00	10.19	20.61	21.61	46.48	98.88
2	34.47	34.27	0.00	0.24	3.39	6.41	7.78	16.37	34.19
wt%			0.00	0.70	9.83	18.60	22.57	47.49	99.19
3	34.44	34.23	0.00	1.72	2.84	6.29	7.17	16.14	34.16
wt%			0.00	4.99	8.25	18.26	20.82	46.86	99.19
4	35.25	35.01	0.00	2.45	3.29	6.24	7.45	15.49	34.92
wt%			0.00	6.95	9.33	17.70	21.13	43.94	99.06
Avg.			0.00	3.16	9.40	18.79	21.53	46.20	99.08

A1: Raw Data from Drop Test

Table 12: Screening analysis drop test 8wt% lignosulfonate axial press

Day 1	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	26.39	26.14	0.00	1.44	2.26	5.16	5.94	11.18	25.98
wt%			0.00	5.46	8.56	19.55	22.51	42.36	98.45
2	24.71	24.51	0.00	1.40	2.96	4.55	6.02	9.43	24.36
wt%			0.00	5.67	11.98	18.41	24.36	38.16	98.58
3	25.5	25.33	0.00	1.54	1.45	4.56	6.33	11.30	25.18
wt%			0.00	6.04	5.69	17.88	24.82	44.31	98.75
4	26.69	26.49	2.23	0.42	3.79	4.61	5.51	9.73	26.29
wt%			8.36	1.57	14.20	17.27	20.64	36.46	98.50
Avg.			2.09	4.68	10.11	18.28	23.08	40.32	98.57
Day 2	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	24.94	24.75	1.64	0.56	3.53	4.39	5.60	8.64	24.36
wt%			6.58	2.25	14.15	17.60	22.45	34.64	97.67
2	23.52	23.34	0.00	1.07	2.37	3.03	6.05	10.56	23.08
wt%			0.00	4.55	10.08	12.88	25.72	44.90	98.13
3	21.23	21.07	0.00	2.09	3.41	3.56	4.62	7.16	20.84
wt%			0.00	9.84	16.06	16.77	21.76	33.73	98.16
4	25.37	25.12	0.00	0.34	3.57	4.47	6.12	10.36	24.86
wt%			0.00	1.34	14.07	17.62	24.12	40.84	97.99
Avg.			1.64	4.49	13.59	16.22	23.52	38.53	97.99

Table 13: Screening analysis after drop test 1wt% bentonite, axial press

Day 1	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	25.35	25.11	0.00	2.38	3.15	4.09	3.56	11.93	25.11
wt%			0.00	9.39	12.43	16.13	14.04	47.06	99.05
2	27.3	27.06	1.54	0.44	4.06	4.81	4.16	12.06	27.07
wt%			5.64	1.61	14.87	17.62	15.24	44.11	99.09
3	26.93	26.65	1.85	1.27	2.71	3.16	4.34	13.34	26.67
wt%			6.87	4.72	10.06	11.73	16.12	49.54	99.03
4	27.13	26.95	1.67	0.81	3.49	3.84	3.61	13.43	26.85
wt%			6.16	2.99	12.86	14.15	13.31	49.50	98.97
Avg.			4.67	4.68	12.56	14.91	14.68	47.55	99.04
Day 2	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	28.52		0.00	2.66	3.19	3.64	4.55	14.19	28.23
wt%			0.00	9.33	11.19	12.76	15.95	49.75	98.98
2	27.91		0.00	2.21	4.10	3.88	4.39	13.08	27.66
wt%			0.00	7.92	14.69	13.90	15.73	46.86	99.10
3	25.89		2.54	0.00	5.02	4.05	3.78	10.24	25.63
wt%			9.81	0.00	19.39	15.64	14.60	39.55	99.00
4	25.93		1.41	0.75	2.94	4.31	4.16	12.08	25.65
wt%			5.44	2.89	11.34	16.62	16.04	46.59	98.92
Avg.			3.81	5.03	14.15	14.73	15.58	45.69	99.00
1 Week	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	25.67	25.4	1.33	0.67	2.43	4.49	4.09	12.41	25.42
wt%			5.18	2.61	9.47	17.49	15.93	48.34	99.03
2	26.39	26.23	0.00	1.21	3.02	4.62	5.20	12.10	26.15
wt%			0.00	4.59	11.44	17.51	19.70	45.85	99.09
3	28.59	28.4	1.71	1.39	2.42	4.05	4.73	14.06	28.36
wt%			5.98	4.86	8.46	14.17	16.54	49.18	99.20
4	25.14	24.98	0.00	2.17	1.65	4.63	4.33	12.11	24.89
wt%			0.00	8.63	6.56	18.42	17.22	48.17	99.01
Avg.			2.79	5.17	8.98	16.90	17.35	47.89	99.08

2 weeks	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	23.38	23	0.00	0.00	0.80	3.15	4.33	14.68	22.96
wt%			0.00	0.00	3.42	13.47	18.52	62.79	98.20
2	23.59	23.37	0.00	0.00	0.92	3.68	4.26	14.47	23.33
wt%			0.00	0.00	3.90	15.60	18.06	61.34	98.90
3	25.57	25.41	0.00	0.51	1.14	4.42	4.34	14.94	25.35
wt%			0.00	1.99	4.46	17.29	16.97	58.43	99.14
4	26.28	26.23	0.00	0.32	1.36	4.09	5.38	15.04	26.19
wt%			0.00	1.22	5.18	15.56	20.47	57.23	99.66
Avg.			0.00	0.80	4.24	15.48	18.51	59.95	98.97
3 weeks	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	25.98	25.76	0.99	0.54	1.56	4.23	4.66	13.72	25.70
wt%			3.81	2.08	6.00	16.28	17.94	52.81	98.92
2	25.79		0.00	0.00	1.88	5.59	5.57	12.54	25.58
wt%			0.00	0.00	7.29	21.68	21.60	48.62	99.19
3	24.96	24.81	0.00	0.00	2.13	5.29	4.90	12.40	24.72
wt%			0.00	0.00	8.53	21.19	19.63	49.68	99.04
4	23.51	23.23	0.00	1.81	2.38	3.72	4.39	10.95	23.25
wt%			0.00	7.70	10.12	15.82	18.67	46.58	98.89
Avg.			0.95	2.44	7.99	18.74	19.46	49.42	99.01
4 weeks	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	28.75	28.57	0.00	0.49	2.78	5.41	6.27	13.56	28.51
wt%			0.00	1.70	9.67	18.82	21.81	47.17	99.17
2	23.49	23.35	0.00	0.70	2.14	4.92	4.71	10.83	23.30
wt%			0.00	2.98	9.11	20.95	20.05	46.10	99.19
3	25.99	25.81	0.00	0.43	1.93	5.75	5.13	12.52	25.76
wt%			0.00	1.65	7.43	22.12	19.74	48.17	99.12
4	27.04	26.77	0.00	0.00	2.76	5.26	5.71	13.02	26.75
wt%			0.00	0.00	10.21	19.45	21.12	48.15	98.93
Avg.			0.00	1.58	9.10	20.33	20.68	47.40	99.10

A1: Raw Data from Drop Test

5 weeks	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	23.83	23.67	0.95	0.00	1.80	4.66	4.74	11.49	23.64
wt%			3.99	0.00	7.55	19.56	19.89	48.22	99.20
2	28.96	28.72	0.00	0.27	2.87	4.45	5.67	15.45	28.71
wt%			0.00	0.93	9.91	15.37	19.58	53.35	99.14
3	27.77	27.57	0.00	0.57	3.29	5.65	5.44	12.62	27.57
wt%			0.00	2.05	11.85	20.35	19.59	45.44	99.28
4	26.09	25.91	0.00	0.83	3.06	4.70	4.92	12.32	25.83
wt%			0.00	3.18	11.73	18.01	18.86	47.22	99.00
Avg.			1.00	1.54	10.26	18.32	19.48	48.56	99.16

Table 14: Screening analysis from droptest 3wt% lime, 6wt% molasses, axial press

Day 1	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	24.52	24.35	0.00	0.64	1.56	5.11	4.98	11.96	24.25
wt%			0.00	2.61	6.36	20.84	20.31	48.78	98.90
2	24.97	24.79	0.00	0.00	2.36	4.65	5.35	12.35	24.71
wt%			0.00	0.00	9.45	18.62	21.43	49.46	98.96
3	21.75	21.56	0.00	0.00	1.57	3.36	4.60	12.02	21.55
wt%			0.00	0.00	7.22	15.45	21.15	55.26	99.08
4	28.03	27.87	0.00	0.00	2.93	5.11	5.95	13.83	27.82
wt%			0.00	0.00	10.45	18.23	21.23	49.34	99.25
Avg.			0.00	0.65	8.37	18.29	21.03	50.71	99.05

Day 2	W. b/drop [g]	W. a/drop [g]	>10 mm	<10 mm	<6.3 mm	<3.15 mm	<2 mm	<1 mm	sum a/screen
1	24.62	24.35	0.00	1.22	1.17	4.30	4.11	13.49	24.29
wt%			0.00	4.96	4.75	17.47	16.69	54.79	98.66
2	25.42	25.17	0.00	0.93	2.32	5.56	5.03	11.32	25.16
wt%			0.00	3.66	9.13	21.87	19.79	44.53	98.98
3	24.43	24.26	0.00	0.32	1.07	4.79	4.52	13.47	24.17
wt%			0.00	1.31	4.38	19.61	18.50	55.14	98.94
4	24.81	24.59	0.00	0.42	2.18	4.83	4.87	12.30	24.60
wt%			0.00	1.69	8.79	19.47	19.63	49.58	99.15
Avg.			0.00	2.90	6.76	19.60	18.65	51.01	98.93

A1: Raw Data from Drop Test

Table 15: Screening analysis from drop test 4wt% lime, 8wt% molasses, axial press

Day 1	W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<2mm	<1mm	sum a/screen
1	24.39	24.28	4.95	5.50	2.57	3.73	3.22	4.07	24.04
wt%			20.30	22.55	10.54	15.29	13.20	16.69	98.56
2	25.61	25.51	5.90	3.93	2.45	4.48	3.47	5.07	25.30
wt%			23.04	15.35	9.57	17.49	13.55	19.80	98.79
3	23.38	23.33	9.34	3.67	2.60	2.91	2.10	2.60	23.22
wt%			39.95	15.70	11.12	12.45	8.98	11.12	99.32
4	22.5		16.45	0.50	1.07	1.42	1.20	1.72	22.36
wt%			73.11	2.22	4.76	6.31	5.33	7.64	99.38
Avg.			39.10	13.95	8.99	12.89	10.27	13.81	99.01

Day 2	W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<2mm	<1mm	sum a/screen
1	22.82	22.8	19.79	1.64	0.24	0.48	0.30	0.29	22.74
wt%			86.72	7.19	1.05	2.10	1.31	1.27	99.65
2	24.75	24.68	11.38	4.87	2.46	2.13	1.65	2.11	24.60
wt%			45.98	19.68	9.94	8.61	6.67	8.53	99.39
3	21.27	21.25	20.73	0.00	0.16	0.03	0.13	0.20	21.25
wt%			97.46	0.00	0.75	0.14	0.61	0.94	99.91
4	23.51	23.46	15.26	1.65	1.75	1.61	1.31	1.74	23.32
wt%			64.91	7.02	7.44	6.85	5.57	7.40	99.19
Avg.			73.77	8.47	4.80	4.42	3.54	4.53	99.54

A1: Raw Data from Drop Test

Table 16: Screening analysis from drop test 4wt% lime, 8wt% molasses, roll pressed

Day 1		W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<2mm	<1mm	sum a/screen
	1	10.92	10.91	4.31	6.25	0.10	0.08	0.05	0.09	10.88
wt%				39.47	57.23	0.92	0.73	0.46	0.82	99.63
	2	11.39	11.38	2.28	8.65	0.17	0.04	0.13	0.09	11.36
wt%				20.02	75.94	1.49	0.35	1.14	0.79	99.74
	3	10.93	10.93	4.10	6.38	0.06	0.15	0.12	0.11	10.92
wt%				37.51	58.37	0.55	1.37	1.10	1.01	99.91
	4	11.05	11.04	2.25	8.49	0.06	0.08	0.07	0.09	11.04
wt%				20.36	76.83	0.54	0.72	0.63	0.81	99.91
Avg.				29.34	67.10	0.88	0.80	0.83	0.86	99.80

Day 2		W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<2mm	<1mm	sum a/screen
	1	12.86	12.85	2.14	10.28	0.12	0.11	0.06	0.10	12.81
wt%				16.64	79.94	0.93	0.86	0.47	0.78	99.61
	2	10.8	10.79	4.14	6.01	0.08	0.27	0.11	0.13	10.74
wt%				38.33	55.65	0.74	2.50	1.02	1.20	99.44
	3	10.88	10.87	6.42	4.09	0.06	0.14	0.05	0.10	10.86
wt%				59.01	37.59	0.55	1.29	0.46	0.92	99.82
	4	10.61	10.61	2.04	8.22	0.08	0.04	0.12	0.10	10.60
wt%				19.23	77.47	0.75	0.38	1.13	0.94	99.91
Avg.				33.30	62.66	0.74	1.25	0.77	0.96	99.69

5 weeks		W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<2mm	<1mm	sum a/screen
	1	21.77	21.74	10.65	10.35	0.13	0.18	0.15	0.26	21.72
wt%				48.92	47.54	0.60	0.83	0.69	1.19	99.77
	2	21.53	21.51	4.25	16.61	0.06	0.19	0.18	0.22	21.51
wt%				19.74	77.15	0.28	0.88	0.84	1.02	99.91
	3	21.62	21.6	8.50	12.42	0.10	0.14	0.21	0.24	21.61
wt%				39.32	57.45	0.46	0.65	0.97	1.11	99.95
	4	21.34	21.32	6.35	14.32	0.17	0.14	0.15	0.20	21.33
wt%				29.76	67.10	0.80	0.66	0.70	0.94	99.95
Avg.				34.43	62.31	0.53	0.75	0.80	1.07	99.90

A1: Raw Data from Drop Test

Table 17: Screening analysis after drop test 8wt% lignosulfonate, roll press

| Day 1		W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<2mm	<1mm	sum a/screen
	1	12.14		6.95	4.56	0.08	0.28	0.06	0.20	12.13
wt%				57.25	37.56	0.66	2.31	0.49	1.65	99.92
	2	12.49	12.48	9.71	2.29	0.28	0.05	0.05	0.11	12.49
wt%				77.74	18.33	2.24	0.40	0.40	0.88	100.00
	3	11.82	11.82	4.54	6.71	0.25	0.15	0.04	0.09	11.78
wt%				38.41	56.77	2.12	1.27	0.34	0.76	99.66
	4	11.67	11.69	6.94	3.83	0.41	0.11	0.14	0.17	11.60
wt%				59.47	32.82	3.51	0.94	1.20	1.46	99.40
Avg.				58.22	36.37	2.13	1.23	0.61	1.19	99.74
Day 2		W. b/drop [g]	W. a/drop [g]	>10mm	<10mm	<6.3mm	<3.15mm	<2mm	<1mm	sum a/screen
	1	12.05	12.04	6.85	4.58	0.29	0.16	0.06	0.10	12.04
wt%				56.85	38.01	2.41	1.33	0.50	0.83	99.92
	2	12.38	12.37	6.89	4.41	0.38	0.31	0.18	0.16	12.33
wt%				55.65	35.62	3.07	2.50	1.45	1.29	99.60
	3	11.84	11.83	9.44	1.41	0.44	0.14	0.17	0.20	11.80
wt%				79.73	11.91	3.72	1.18	1.44	1.69	99.66
	4	12	12	4.55	6.74	0.20	0.24	0.12	0.14	11.99
wt%				37.92	56.17	1.67	2.00	1.00	1.17	99.92
Avg.				57.54	35.43	2.71	1.75	1.10	1.24	99.77

A2: Additional Images
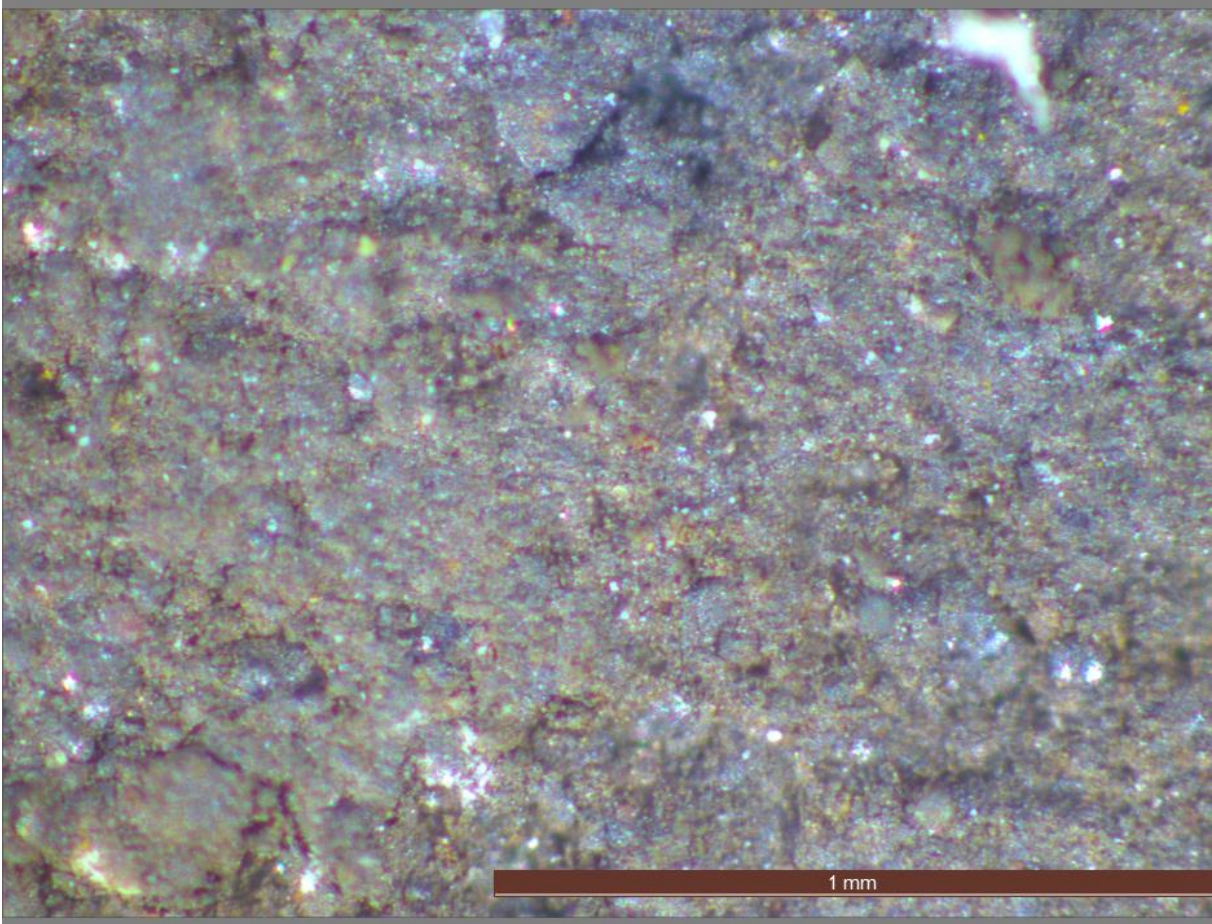
Figure 46: Macro image, 1wt% bentonite 32x

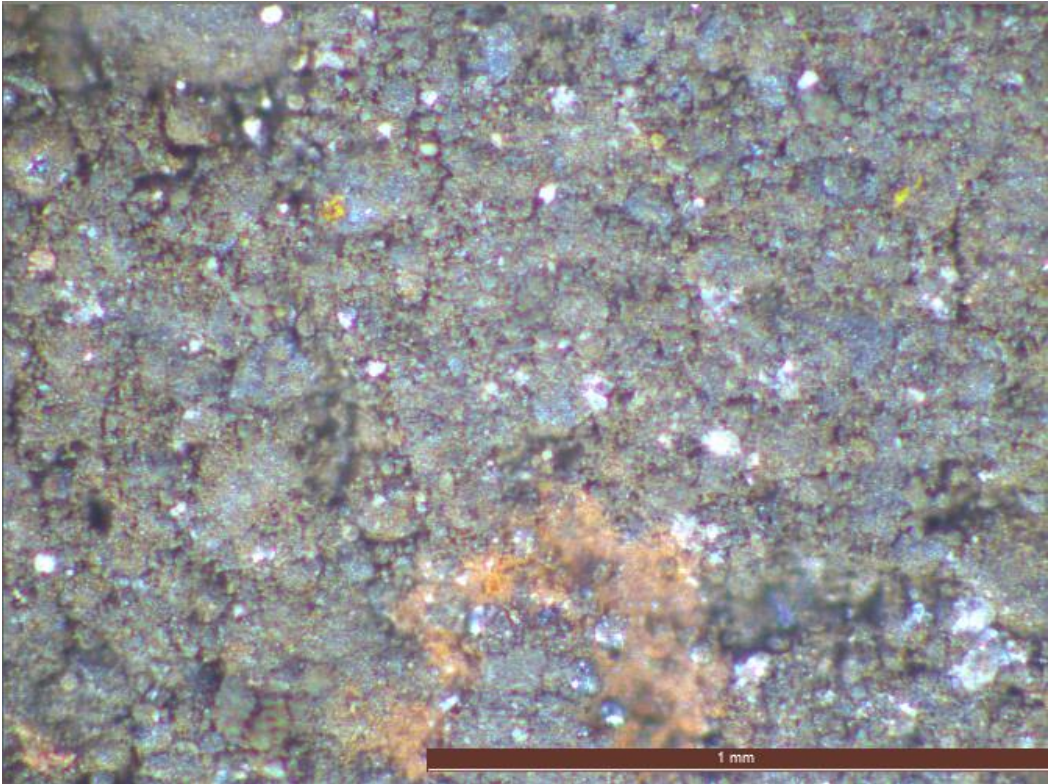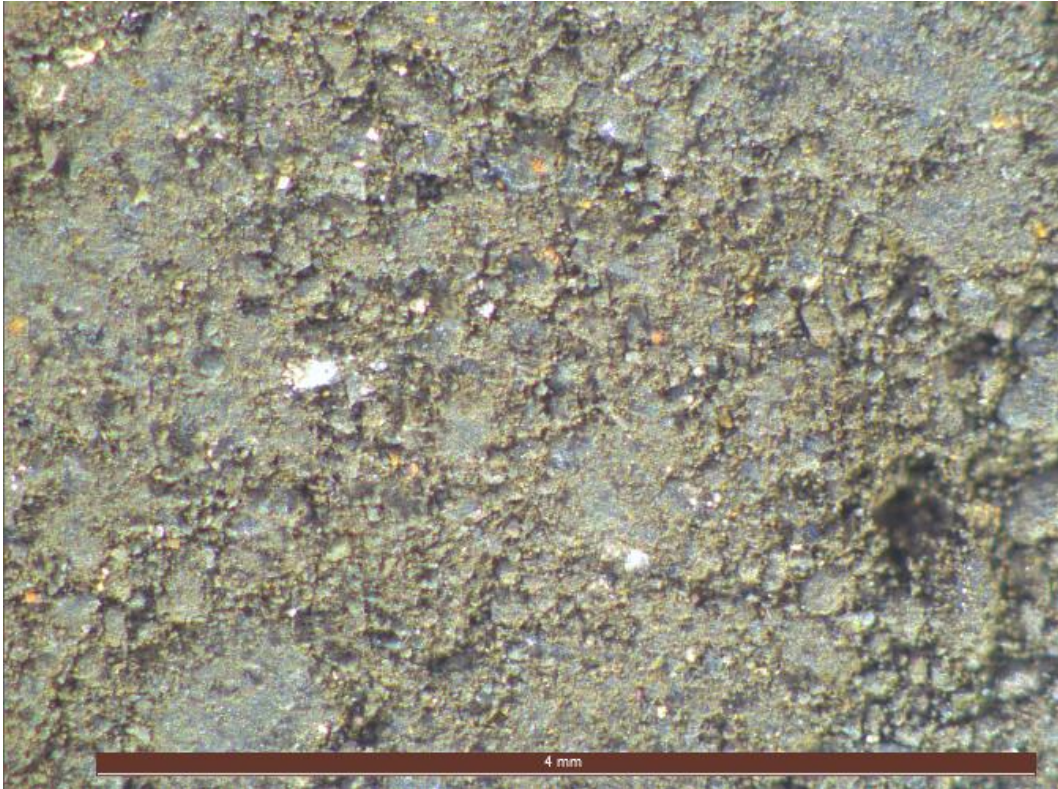**Figure 47: Macro image 4wt% lignosulfonate, 32x**
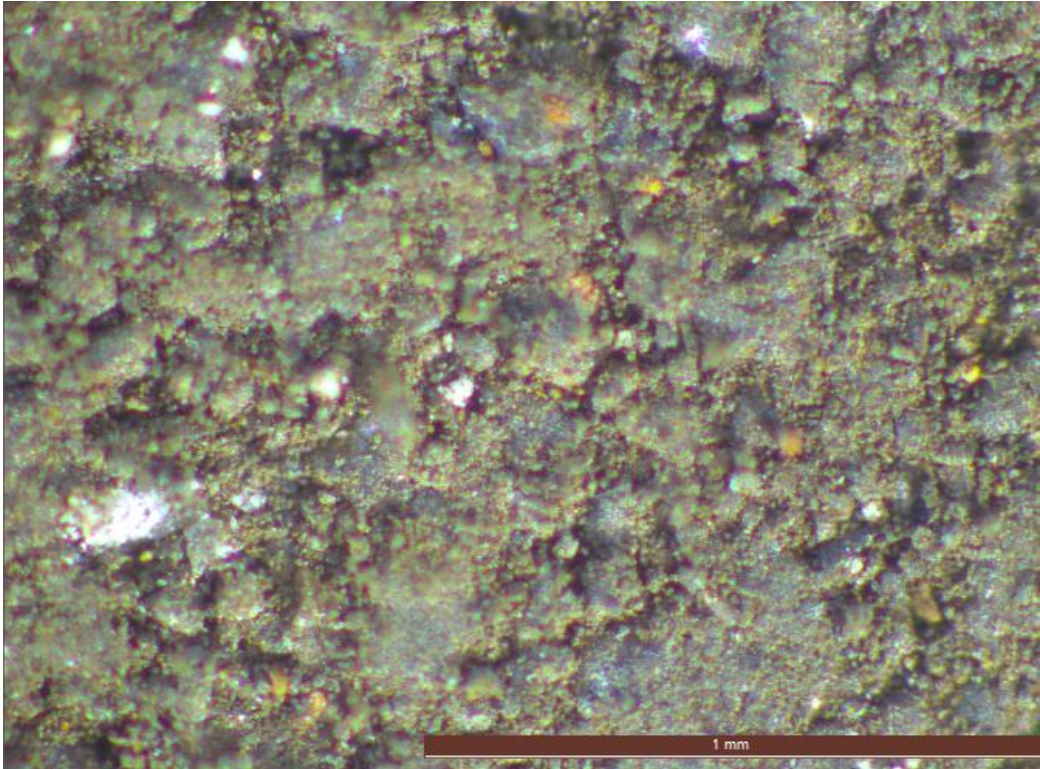

Figure 48: Macro image 6wt% lignosulfonate, 16x

Figure 49: Macro image 6wt% lignosulfonate, 32x

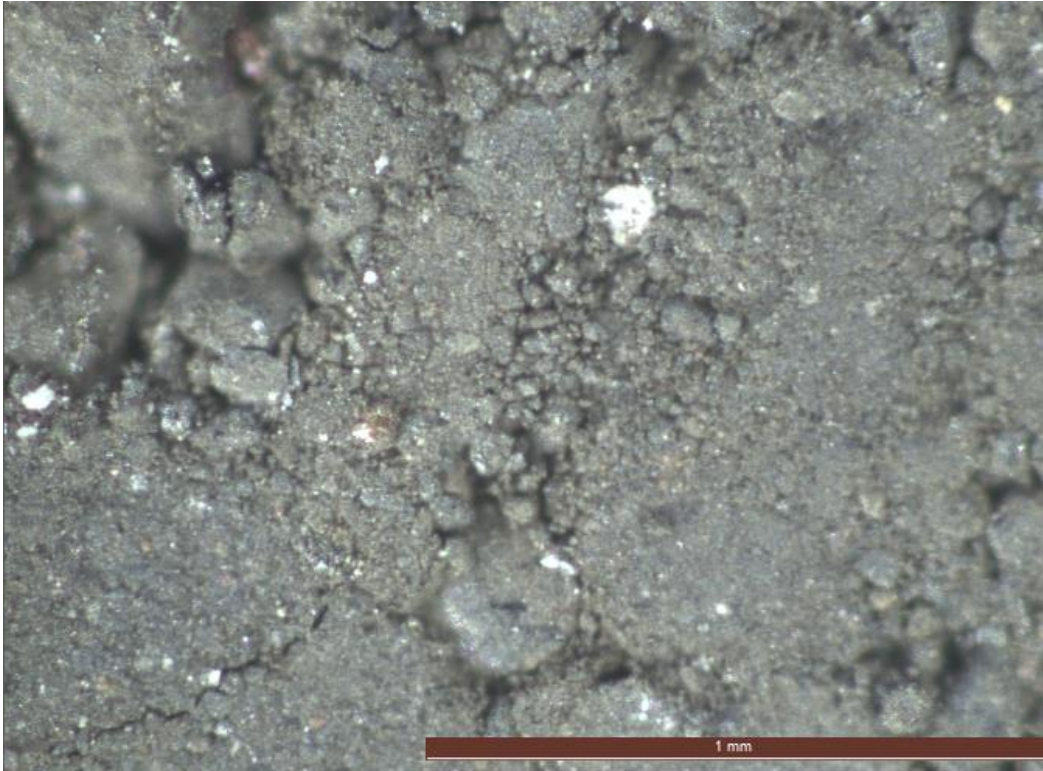**Figure 50: Macro image 8wt% lignosulfonate, 16x**
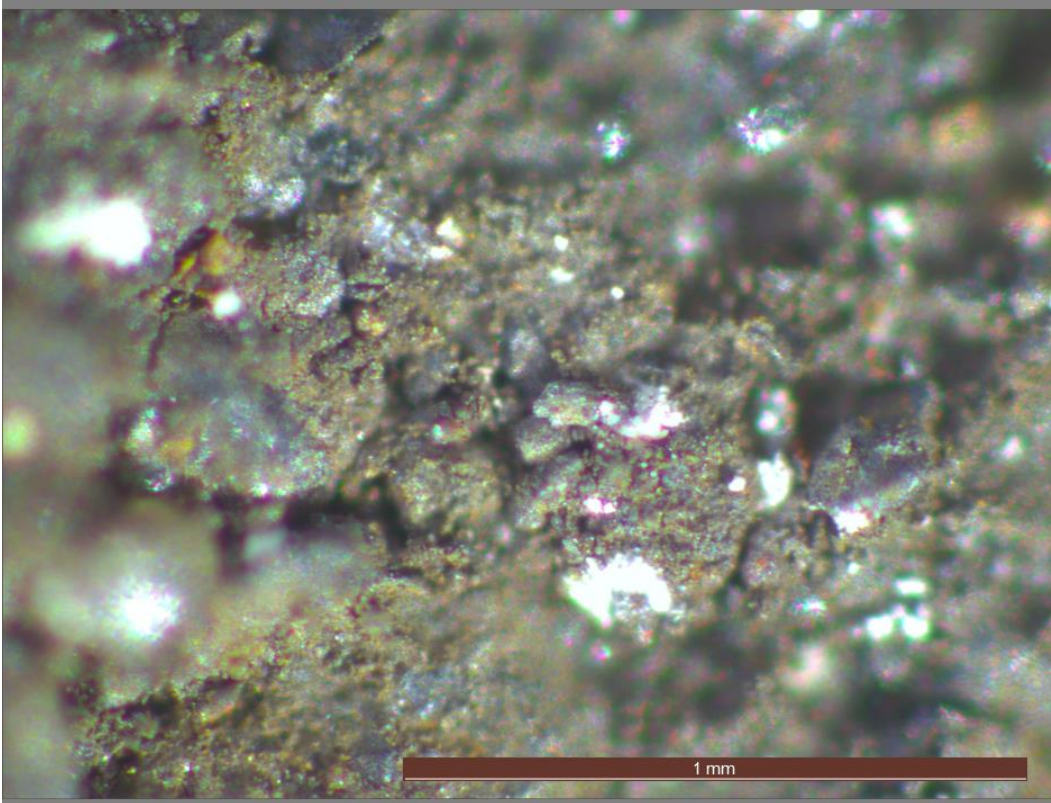
Figure 51: Macro image 8wt% lignosulfonate, 32x

Figure 52: Macro image 4wt% lime, 8 wt% molasses, 32x