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DRYING METHODS AND TESTING FOR RESIDUES

Boliden Kokkola

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The purpose of this thesis was to determine if it is feasible to dry sludge in outdoor conditions using floor heating, and what problems have to be overcome to make it possible. The work was commissioned by Boliden Kokkola Oy. The theory part focuses mainly on drying as a physical phenomenon and on industrial drying. The experiments for this work were done in two ways, outdoors with a floor heating provided by a thermal power station and in a laboratory using heating plates. The objective for these experiments was to see how fast the compound residue and zinc ferrite would dry in outdoor conditions compared to indoor conditions. The results are presented in more detail in the experimental part.

The tests showed that drying outdoors is very inefficient with very little drying occurring, due to the low temperature and high humidity of the surroundings during October and November, when these experiments were conducted. Drying was much more efficient in the laboratory, where the desired humidity of 10-14 % was achieved in 10 to 20 hours, depending on which of the used residues was being dried. What made drying possible in the laboratory was that the temperature was constantly around normal room temperature at 20°C and there was sufficient air ventilation.

Results of the tests showed that an arrangement, which ensures constant temperature of at least 20°C for the surroundings, is needed for drying to occur. The required energy could be obtained from the exit gases of various parts of the zinc production process, using an exit gas washer, or from the surplus energy of returning water from district heating.

Key words

evaporation, humidity, sludge, vapor pressure

CONCEPT DEFINITIONS

Anode an electrode in an electrochemical pair where oxidation occurs

Cathode an electrode in an electrochemical pair where reduction occurs

Compound residue a residue leftover from leaching, mostly made of jarosite

Condensation point temperature at which vapor condenses in to liquid form

District heating a form of heating based on circulating hot water in long pipes

Exit gas washer a washer that utilizes the waste heat from exit gases

Partial pressure pressure caused by a single gas in a mixture of gases

Refrigeration agent fluid or gas that absorbs heat

Residue material left over from a chemical reaction

Vapor gas in a temperature where the substance can also be liquid or solid

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1 INTRODUCTION

This thesis was commissioned by Boliden Kokkola Oy. Boliden Kokkola is a smelter mainly producing zinc and also other materials, like sulphuric acid and silver concentrate. The purpose of this thesis is to explore the possibility of using floor heating to dry or at least pre-dry sludge in outdoor conditions for further use. The primary focus is on drying as a phenomenon, and on how drying is performed in industry. Multiple experiments were conducted while making this thesis, first with floor heating using a thermal power station and then in a laboratory with heating plates. The experiments consisted of drying the sludge in different temperatures and measuring the humidity every now and then to see how fast the sludge were drying. The drying in the experiments was conducted on zinc ferrite and compound residue, the tests were conducted from October to January.

The hypothesis when the experiments were started was that when the sludge is heated from the bottom, it will dry with a certain speed in a certain temperature. The experiments were performed to verify an optimal temperature for the drying.

2 BOLIDEN KOKKOLA

The purpose of this chapter is to explain the zinc production process of Boliden Kokkola by briefly going through the main phases of the process.

Zinc production was started in Kokkola in 1969 by Outokumpu Oyj. Yearly production at that time was 80 000 tonnes, the smelter was bought by Boliden AB in 2004. Currently Boliden Kokkola is the second largest zinc producing smelter in Europe, with an annual output of 315 000 tonnes. In addition to pure zinc, the smelter also produces sulfuric acid, silver, gold and lead. The parent company of Boliden Kokkola is Boliden AB, which is one of Europe's leading companies in the field of metal industry. Ore used in Boliden Kokkola zinc production process comes from Boliden owned mines in Sweden and Ireland. In addition to owning Boliden Kokkola, Boliden AB also owns a copper smelter in Harjavalta and a copper, gold and zinc mine in Kylylahti, Finland. (Lahti 2013, 3-4.)

2.1 Zinc production process

The main phases of the zinc production process in Boliden Kokkola are roasting of the concentrate, leaching, purification, electrolysis in the cell house and foundry (FIGURE 1). Sulphuric gas coming from the roasting process is directed to the sulphuric acid plant for the production of sulphuric acid. The surplus energy left over from the creation of sulphuric acid is directed to Kokkolan Energia power plant for the production of district heating. Copper and cobalt containing sediment from the purification process is sent to Harjavalta copper smelter. In 2014 Boliden Kokkola started salvaging the silver concentrate found in zinc concentrate by establishing a silver recovery facility to the area, the salvaged silver is then sold to other metal smelters as silver concentrate. Zinc concentrate used in the production of zinc comes primarily from multiple foreign mines to Kokkola deep water port, from where it is transferred trough a weighing station and a sampling station to a storage. Concentrate coming from the Kylylahti mine is brought directly to the storages by trucks. (Korhonen-Helander, Willman 2015, 3-4.)

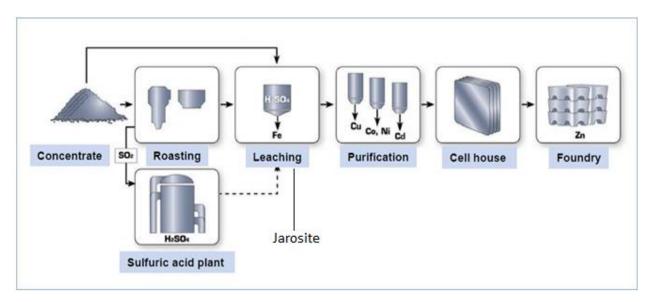


FIGURE 1. Boliden Kokkola zinc production process (Boliden Kokkola)

2.1.1 Roasting

Roasting means dissolving a compound into oxides or other useful compounds by combustion. In Boliden Kokkola the compounds in roasting are mainly zinc sulfides (ZnS), which are dissolved by combustion to an oxidic form (ZnO) so the zinc is in a more easily dissolving form for the next phase, leaching. Used compounds contain 45-60% zinc and 30% sulphur. Sulphur is collected from the sulfidic zinc concentrate and transferred to the sulphuric acid plant (Korhonen-Helander & Willman 2015, 4-5.)

2.1.2 Leaching

In leaching the zinc calcine formed in the roasting phase is dissolved into the sulphuric acid coming from electrolysis, at about 80°C, forming a zinc sulphate. After leaching the iron from the zinc sulfate is precipitated and filtered from the solution in the form of jarosite, and the leftover silver is collected. (Lahti 2013, 6; Rasinmäki 2018, 5)

2.1.3 Purification

After leaching the zinc sulfate still contains small amounts of impurities such as copper, cobalt, nickel and cadmium, which need to be precipitated from the solution before electrolysis. Purification is based on a 3-phase continuous process, where more noble metals than zinc are reduced and precipitated using zinc powder. After purification the zinc content of the zinc sulfate solution is 150g/l. (Korhonen-Helander, Willman 2015, 4-5.)

2.1.4 Electrolysis

After purification the zinc sulfate solution is pumped into pools containing cathode-anode cells. Aluminium plates act as the cathode and lead plates as the anode. Zinc is separated from the solution by using electric currents, reducing the zinc to precipitate on to the surface of the aluminium plates. The zinc continues to accumulate for 36 hours, after which the zinc layer is thick enough and the aluminium plates are changed to new ones. Zinc is separated from the plates using automatic stripping machines and moved to a storage room before melting them into zinc ingots. The separated cathodes are about 99,995% pure zinc. (Lahti 2013, 6.)

2.1.5 Foundry

Zinc plates are then moved from the storage in bundles weighing 1 or 2 tonnes, into a smelting furnace by using conveyors and feeding shafts. There are 2 ovens used in the melting of the zinc. The ovens are similar and both have a capacity of 75 tonnes, both ovens are heated by 6 coils and have a melting capacity of 25 tonnes/h. Temperature of the zinc is kept at 490-520°C, well past the melting point of zinc, which is 419,3°C. Molten zinc is transferred into moulding targets, by moving it into gutters using electrical centrifugal pumps. The zinc is then moved into chill moulds via a distributor. After the distributor a skimming robot removes the slag from the surface of the molten zinc, after which the ingots pass between cooling water nozzles, where the chill moulds are cooled from above and under. Detachment hammers then release the ingots from the chill moulds, after which ingots are transferred into cooling conveyors (Lahti 2013, 7-10.)

3 PRINCIPLES OF DRYING

Drying is one of the oldest and most common operations in chemical engineering. Drying is also one of the most energy consuming unit operations in chemical engineering, due to the high waste heat of vaporization and high inefficiency of hot air as a drying medium. Energy consumption varies from 5% in chemical process industries to 35% in paper industry. Drying as a unit operation involves converting solids or sludge into a completely solid product by evaporating the liquid from the original substance by using heat. Drying is used in multiple industries, including the chemical, agricultural, biotechnology, ceramics, as well as pulp, paper and wood processing industries. In drying, multiple possible factors have to be taken into account, like potential unwanted transformations, such as contraction, crystallization or glass transitions. Sometimes the substance can also change colour, texture or odour. Drying can be done in a variety of circumstances to many differing materials. Drying time can range from less than a second for tissue paper to up to 5 months for some hardwood species. Production capacity can also range from 0.1 kg/h to 100 t/h. (Mujumdar 2002, 1-3.)

When heating a material, water rises to its surface. The speed of evaporation is stable when the surface stays moist. Factors that affect the speed of drying include evaporation on the surface, hydrostatic pressure between the surface and atmosphere, and the speed of moisture rising towards the surface from inside the substance. (Mujumdar 2002, 1-3.)

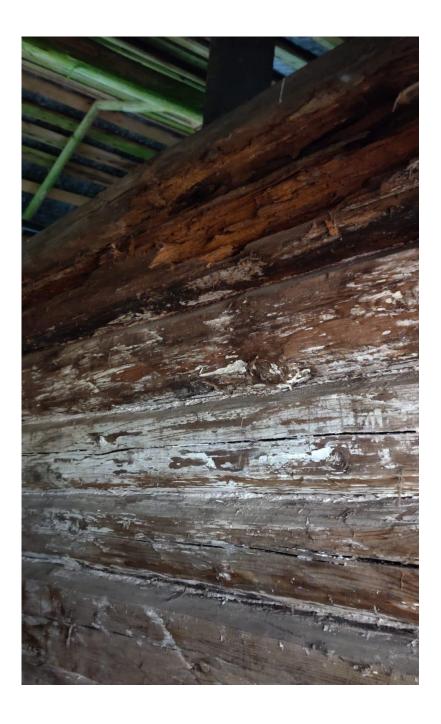
Materials that are dried strive towards a balance in humidity with the surrounding air. If the surrounding air is drier than the material, it dries on its own. Drying can be sped up by heating the material, which causes pressure to rise and push the humidity from the structure, by heating the surrounding air, which increases the ability of air to receive humidity, or by creating air flow around the structure, which removes humidity. (Kuivatuksen suunnittelu ja toteutus 2015.)

3.1 Purposes of drying

Drying has been used to preserve food for thousands of years. When moist, biomaterials rapidly begin to spoil due to microbe activity and enzyme functions, which generates humidity and heat. Biomaterials are dried to prevent microbes from getting water they need for growing, thus preventing the food from spoiling. (Viita 2013, 8.) Many factors contribute to the growth of microbes in addition to humidity, such as temperature, the concentration of oxygen, acidity and the physical condition of the material. When wheat is harvested, its humidity is usually between 20-40%. In order to preserve wheat for a long time, it is usually dried to a humidity of ≤14%. (Kivinen 2019, 8.) If the humidity of surrounding air exceeds 62%, it is possible for fungi to form in biomaterials, or if the air humidity exceeds 90%, bacterial growth becomes a possibility. If the humidity of wheat is over 30%, it begins to spoil in 24 hours and drying has to be started swiftly. Problem with drying wheat is that if even one spot in the stack begins to spoil, it begins to spread and spoil even more of it. (Ahokas 2014.)

Some substances are required to have a certain moisture to be allowed on cargo ships. This moisture content is called transportable moisture limit (TML) and it is measured on liquefying substances. If a substance is moister than this limit allows, there is high risk of the ship capsizing due to the solid cargo liquefying on board, liquefaction can happen on the materials because of the vibration of the ship's engine and wave motion of the ship on the seas. (Transportable Moisture Limit Testing 2021.)

Wood is technically unusable if it is not dry, it usually dries slowly on its own to a certain humidity. If wood is used when it is still too moist, or if it is continuously exposed to water it starts to decay, which can then cause some serious structural damage (PICTURE 1). Drying has to be carried out in a way that ensures that it happens as evenly across the wood as possible, also differences in moisture between wood objects have to be as low as possible. Drying can also cause cracks to form inside or on the top of wood. In wood industry the moisture of wood is measured as the amount of water (%) from the weight of dry wood. (Puutavaran kuivaus 2003.)



PICTURE 1. Rotten and partly damaged wood caused by humidity.

3.2 Factors in drying

The purpose of drying is to rid the structure of as much water as possible. There are multiple factors which affect drying in one way or another. Some circumstances that affect the speed of drying are humidity and temperature of the surrounding air, humidity and weight of the dried material, and the physical conditions of the material. As the drying progresses, it also slows

down consuming more and more energy. The surrounding air also has to be dry enough and has to be blown away constantly for drying to occur. If the surrounding air is dry enough, humidity from the object can transfer to the air. (Viita 2013, 11.)

Moist material consists of dry substance and water. The humidity can be reported in relation to total mass or to the dry mass. When talking of humidity in relation to total mass, the abbreviation wet basis (w.b) is used, when referencing water in relation to dry mass, the abbreviation dry basis (d.b) is used. (Holmberg 2017, 8-13.)

A drying process has three main phases, which are transient early stage, constant rate period and falling rate period. (FIGURE 2.) In the transient early stage, the temperature of the material rises to the corresponding wet-bulb temperature of surrounding air. Wet-bulb temperature depends on the temperature of air, humidity and pressure. Transient early stage is usually brief compared to the rest of the drying process and during this phase there is very little drying, which is why it is not shown in FIGURE 2.

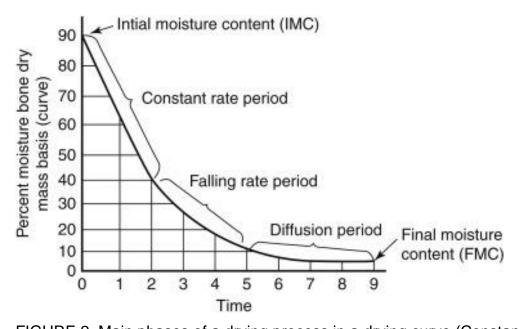


FIGURE 2. Main phases of a drying process in a drying curve (Constant Rate Period 2016.)

When the material has reached its wet-bulb temperature, the constant rate period begins, during which humidity begins to evaporate from the surface, but the surface stays moist due to capillary action. During the constant rate period, the amount of moisture rising to the surface

is greater than the speed of evaporation, and drying is only slowed down by the boundary layer of air and vapor.

When the humidity of the material decreases beyond a certain point, humidity does not rise to the surface fast enough anymore, causing the surface temperature to rise. The falling rate period then begins, during which drying slows down considerably. Also during this phase evaporation is slowed down by the inner properties of the material, like the heat transfer coefficient, which describes the amount of power that is transmitted in relation to surface area, and the diffusion factor, which is a physical constant dependent on the molecular size and on other properties like temperature and pressure. When the vapor pressure of the material decreases to the same level as the vapor pressure in the surroundings, drying grinds to a halt. (Silvola 2017, 10-11; Holmberg 2017, 57-58.)

3.2.1 Water

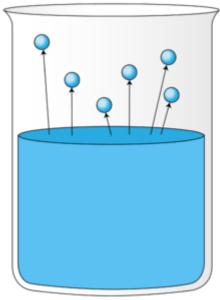
Water (H₂O) is the most common chemical compound on earth, covering around 70% of the surface of earth. Water molecules consist of two hydrogen atoms and one oxygen atom. The bonding of oxygen and hydrogen causes a small charge distribution in the molecule, the hydrogen atoms of the molecule have a positive charge and the oxygen atom has a negative charge. Because of this water molecules are slightly bent, which enables them to bond together with weak hydrogen bonds. Even though these hydrogen bonds are relatively weak, they are strong enough to cause a high boiling point for water in relation to its molecule size. It is also these hydrogen bonds that cause capillary action with water, due to adhesion being greater between the water and container the water is in, than the cohesion between water molecules. Water has great surface tension due to the attraction between water molecules, which causes the round shape of water drops. Water also has great dissolving ability, which is why it is almost never completely pure but there are always some other compounds dissolved into it, this major dissolving ability being the result of the polarity of water. Water is also a great conductor of electricity because salts that are dissolved in water increase its conductivity. (University of Jyväskylä 2013.)

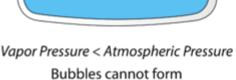
Water can be classified as hard or soft, hard water contains calcium- and magnesium salts that are dissolved into it. Hard water can cause multiple problems, like clogging water pipes by forming calcium deposits inside them. If water is too soft and acidic, it can corrode water pipes from the inside, which will dissolve calcium and iron compounds into the water, colouring it and altering the taste. (University of Helsinki, chapter Veden kovuus 2021.)

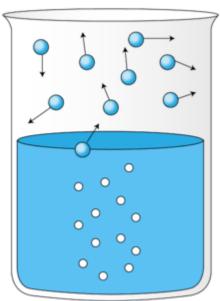
When water vaporizes, the distance between molecules increases. The difference between evaporation and vaporization is that evaporation occurs only on the surface of water and does not require heat to happen, vaporization on the other hand is when water turns into a gas after enough energy is applied (FIGURE 3). Overcoming the attraction between water molecules requires energy, the amount depending on the starting temperature. Water molecules are constantly moving between the air it is in contact with and the body of water itself. When water is heated, the amount of molecules moving to the air slowly becomes greater than the amount of molecules moving to the water. The difference between molecules moving between the air and water is called net evaporation. Evaporation can only occur if vapor pressure on the surface of water is greater than above the surface. Water vapor moves from a greater partial pressure of water vapor to a smaller partial pressure. Greater difference between the pressures on different parts of the object means more intense flow. Air directly above the surface also has to constantly be blown away, or it becomes saturated, ending evaporation completely after some time. (Laine 2020, 3-5.)

Evaporation

Boiling







Vapor Pressure = Atmospheric Pressure

Bubbles can form and rise

FIGURE 3. Comparison between evaporation and vaporization (Similarities Between Evaporation and Boiling 2017.)

3.2.2 Capillary action

Capillary action is defined as the movement of a liquid upwards within a physical body it is in, because of adhesive and cohesive forces interacting between the liquid and the surface of the object. The amount of liquid raised is determined by the diameter of the container and gravitational forces. Due to capillary action, pressure just below the curved surface of water is lower than the air pressure inside the tube, causing water to rise upwards. Air pressure inside the thin tube presses the water in the middle, causing the water to rise. Although water behaves in this way not all liquids do, for example mercury will not climb upwards in a slim tube, due to mercury having a higher cohesive force than adhesive force (FIGURE 4). Cohesion means the

attraction of molecules to other molecules of the same substance. Adhesion on the other hand means the attraction of molecules to other substances. (Peiris, Stein 2020; Holmberg 2017, 45.)

When drying, capillary action causes the moisture to rise to the surface where it evaporates. Common example of capillary action is to show how water rises in a slim tube above the surrounding surface of water. Attraction between molecules of the water and container pushes the water to bend upwards against the container, however surface tension of the water strives to straighten the surface. As these forces are acting, the water rises upwards so the upwards dragging force is in balance with the weight of the water. (Schauman 2012, 17.)

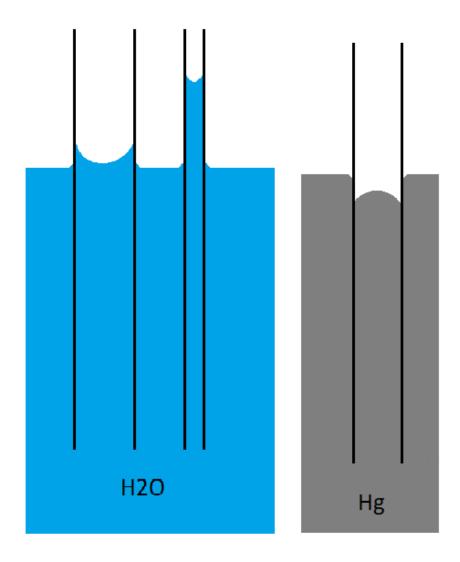


FIGURE 4. Capillary action with water and quicksilver.

3.2.3 Air properties

Humid air is a mixture of dry air and water vapor. Air is mostly composed of nitrogen and oxygen. The absolute humidity of air means the ratio of water vapor compared to the amount of dry air. Air of a certain temperature has a maximum humidity, which is called a condensation point. If the amount of water vapor goes over this maximum amount, the amount of humidity exceeding the maximum amount condenses, so the maximum humidity is reached again. This amount of humidity depends mostly on the air temperature and somewhat on the partial pressure of the air, usually the impact of the partial pressure of air is very minor and does not have to be considered. The speed of drying is affected by the temperature and humidity of the surrounding air. If humidity is low the drying will be faster, focusing air flow to the surface of the object will accelerate the evaporation, whereas if the temperature of the air is high, more evaporated water can fit into it. (Holmberg 2017, 8-13; Laine 2020,3.)

Air humidity is usually expressed in 2 different ways absolute humidity, which indicates how much water is in a cubic meter or kilogram of air (g/m³ or g/kg), and relative humidity, which tells how much humidity there is in the air in percentages of the maximum humidity. (Sisäilmayhdistys ry 2020.) Water vapor is lighter than air, so moist air is also lighter than dry air, which is why humidity rises upwards. For example, completely dry air at 21°C has a density of 1,20 kg/m³, while air at the same temperature with 10 g/kg water content has a density of 1,193 kg/m³. (Karkiainen 2019.)

Total air pressure is the combined pressure of the different gases in the air (oxygen, nitrogen, water vapor, carbon dioxide etc.) average air pressure is 1 atm or 101,325 kPa. Differences in air pressure move the air from a higher air pressure to an area of lower pressure, transferring water vapor and other impurities with it. (Sisäilmayhdistys 2008.)

If dry air and water vapor are presumed to be in an ideal state, absolute humidity can be calculated by using the partial pressure of water vapor and the total pressure of air.

$$X = 0.622 * \frac{P_h}{P_{tot} - P_h}$$
 (1)

The numerical value 0,622 in the equation (1) stands for the ratio of molar masses of water vapor and dry air, 18 g/mol / 29 g/mol = 0,622. If some other substance is used instead of dry air, then the relation of molar masses of the substance in question and water vapor has to be used. (Holmberg 2017, 8.)

3.2.4 Vapor pressure

Vapor pressure is caused by particles in a vaporized state that are above the liquid or solid substance. It also indicates the tendency of the material to transform into vapor, and it increases when temperature rises. (FIGURE 5.) If vapor pressure is greater on the surface than directly above it, the substance loses moisture, greater the difference the faster drying occurs. If vapor pressure is greater above the surface, water vapor condenses back to liquid form. When the relative humidity of the surrounding air is 1, the vapor pressure of the material settles down to the value of the surrounding air and drying cannot occur. When the temperature of the material stays constant, vapor pressure of the bound water decreases at the same speed as the humidity ratio decreases. When there is free-floating water in the material, vapor pressure depends solely on the temperature of the material. If there is only bound water, value of vapor pressure depends in addition to temperature on the humidity ratio of the material. As vapor pressure in the surrounding air of the material is changed, the humidity of the material settles to a new balance. (Holmberg 2017, 30-32.)

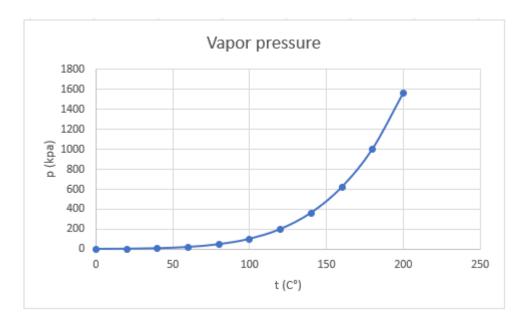


FIGURE 5. Vapor pressure in different temperatures.

3.3 Drying methods

When planning by which way a material is dried, many factors have to be considered such as quality requirement for the product, properties of the raw material, economic factors, drying conditions and maintenance needs. The selected drying method should be as cheap as possible and deliver the required quality of the product. Some methods can be too expensive for some products but reasonably priced for others. Quality requirements can vary greatly depending on the desired product, quality is required to be high in medicinal industries, but in biofuels the requirements for the product can be solely regarding the maximum variation of humidity in the final product. (Holmberg 2017, 185-188.)

There are three main ways for energy to be transferred, which are conduction, convection and radiation. In conduction, heat is transferred between substances that are indirectly in contact with each other, energy then being transferred from the hotter substance to the colder. When heated, the particles vibrate faster and cause surrounding particles to vibrate faster as well. This method is suitable for very moist or thin substances. In convection the energy is transferred directly to the substance, bonding the heat to the substance. Convection is suitable for the drying of solids, liquids or particles. (Kujala 2014, 10-11.)

Most drying applications are based on convection, the drying gas usually being air. In indirect drying transferring heat onto the material is based on conduction, where the heat is transferred into the material through a heat conducting wall. Sometimes the main way to transfer heat is based on radiation. (Holmberg 2017, 56.)

There are two main ways of drying via radiation, which are infrared and dielectric radiation. Infrared radiation is used in the drying of surface layers and membranes, and it cannot be used to dry thick layers. Dielectric radiation uses micro and radio waves, the main source for the energy coming from the electric grid. (Kujala 2014, 11.)

3.3.1 Hot air dryer

Using hot air is the most common method of drying, it works by evaporating the moisture from the surface of the substance. This method has its downsides, depending on the substance which is dried, heat increases the risk of forming mould or fungi. Using hot air also increases the risk of corrosion inside the used equipment. The heat can also damage the product, so proper measures have to be taken to make sure that the equipment and product are not damaged. (Kuivaaminen teollisuudessa 2021.)

When drying using hot air, the air brings the energy required for vaporization to occur. Bringing in dry and hot air also removes the vaporized water from the vicinity. The main components of a hot air dryer are a drying chamber, a heat source and a fan to circulate the heated air (FIG-URE 6). The drying chamber is usually at least partially enclosed to prevent hot air from leaking to the environment, it should also be durable due to it being in constant contact with humidity. The fan blowing the hot air is at the greatest risk of particle contamination due to its moving parts, also it has to endure high temperatures caused by the returning air. (Drying – Basic Hot Air Dryer Design 2013)

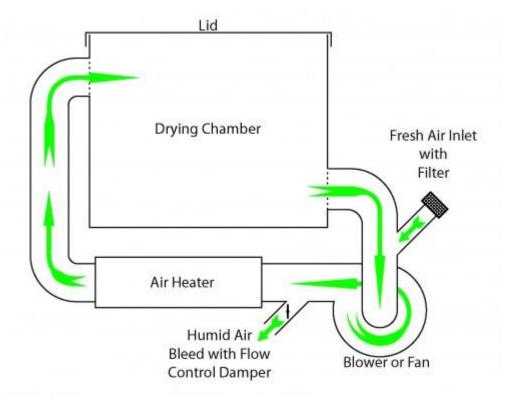


FIGURE 6. Representation of a basic hot air dryer (Drying – Basic Hot Air Dryer Design 2013.)

3.3.2 Contact drying

Contact drying with steam heated cylinders (FIGURE 7) is the most widely used drying method for drying paper, and it has remained relatively unchanged since it was first used for paper drying. There are many different types of contact dryers, such as air floating dryers and single-sided air-impingement dryers. Air floating dryers have webs that are supported on both sides by air jets or cushions. Single-sided air impingement dryers are useful when only one side is to be dried. The main reasons contact drying is predominantly used in paper drying is because it prevents cross-machine shrinkage, and it is a cost-effective method in terms of energy efficiency, also mills such as pulp mills can produce a surplus of steam, which can then be used by the drying section. (Karlsson 2010, 19, 21.)

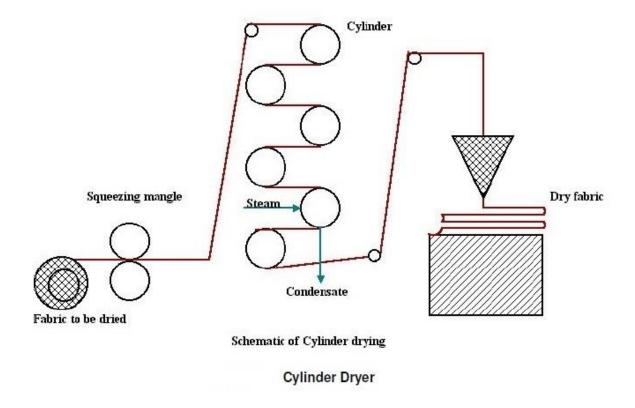


FIGURE 7. Contact drying with a cylinder dryer (Contact drying- Steam cylinders/cans.)

3.3.3 Adsorption drying

Adsorption drying works by taking advantage of the ability of a substance to bind water molecules to its surface and a continuous regeneration process of the water binding substance. Adsorption dryers are also capable of drying air and then returning the air back to the same space. When using adsorption dryers, the temperature does not have to be so accurate, it can function in many different temperatures, including sub-zero temperatures.

There are many kinds of adsorption dryers which all function in different ways. When separating water from pressurized air, an adsorption dryer with two containers of dehydration agent can be used. Air is then first conducted into the first container, when the dehydration agent is saturated, the flow is directed through the other container, meanwhile the dehydrating agent in the first tank is refreshed using electric currents and warm airflow. By using this method, a condensation point between -30 - -90°C can be achieved. The drying agent used in this

method is silica gel, which has a structure that can bind humidity. Sometimes orange agent is added to the silica gel that turns green when it adsorbs humidity, because white silica gel does not change colour or appearance even when it is moist. (Laine 2020, 12; Willman 2015, 64.)

3.3.4 Condensation drying

The functioning of a condensation dryer is based on lowering the temperature of the dried air below the condensation point, so the water vapour in the air is condensed and can be drained into a container. There is a closed refrigeration system in a condensation dryer where the refrigeration agent is first squeezed using a compressor and a choke valve, raising its temperature. The liquid then passes through the choke valve into an evaporator, where the temperature of the liquid decreases because of the pressure dropping. Refrigeration agent then passes back to the compressor, starting the cycle again from the start. The dried air passes in its own district, through the evaporator and the condenser. When moist air arrives into the evaporator, its temperature rapidly decreases below the condensation point, condensing part of the moisture and moving it to a container. Finally, the air is directed to the condenser, where it warms up back to normal temperatures. Condensation dryer is suited for spaces that are very moist and have a temperature of 20-30°C. In these conditions, a condensation dryer functions more efficiently than an adsorption dryer. Condensation dryers are highly dependent on the circumstances of its surroundings, and its functioning weakens considerably when temperature decreases. (Laine 2020, 16-17.)

3.3.5 Spray drying

Spray drying is one of the most used drying methods in industry. In spray drying liquid is sprayed as small drops into a hot gas stream. Solvent in the liquid then evaporates, forming small particles from the substance that is mixed with the liquid. Dry particles are then separated from the gas stream, leaving only a fine powder or granules after which, the desired product makes its way with the air current to a receiver. The nozzle adjusts the substance into small droplets and spreads the droplets evenly in a process known as atomization. Atomization is a

very crucial step for the following phases, breaking the solution into small droplets vastly increases their surface area, which increases the heat and mass transfer between the gas and liquid particles. They are then mixed in the column with the drying gas and the liquid is dried from the droplets. If the droplets are too large they will not dry properly, or if they are too small the temperature of the sprayed substance can rise too high. Dried particles then accumulate at the bottom of the cyclone or into a receiver. (FIGURE 8.) (Kolu 2013, 2-4.) Spray drying is used to generate round and small particles. It is a fast and efficient way to produce dry powder. It is also a continuous process and can easily function on large scales. (Murto 2018, 14-15; Santos etc. 2017.)

In spray drying, high temperatures and the large surface area compared to the volume of the droplets causes them dry rapidly. Because the spray drying process is so fast, the temperature of the particles does not have enough time to rise to the level of the inlet temperature, preventing damage on heat sensitive materials. When the particles come into contact with the inlet temperature they are not dry yet, so it takes a lot of energy for water to vaporize, which protects the particles from the heat. Spray drying is thus suitable for drying sensitive materials, such as proteins. When drying sensitive materials, it is important to make sure that the outlet temperature does not rise too high, because the particles are in that temperature for a long time. (Kolu 2013, 2-4.)

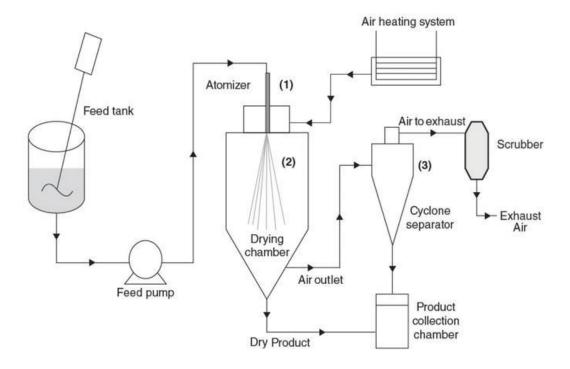


FIGURE 8. Representation of a spray drying mechanism (Santos etc. 2017.)

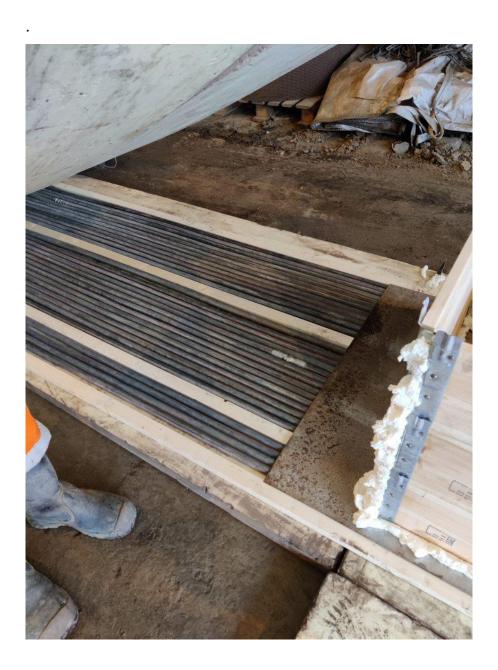
4 EXPERIMENT

The purpose of the experiments was to see if it was possible to dry sludge in large quantity in contact with outside air using floor heating. The floor heating was achieved by using a Heatwork HW1800 thermal power station (PICTURE 2), which runs on diesel. The power station was rented by Boliden. There were hot tubes circulating heat transfer oil coming from the power station, which went under aluminium plates (PICTURE 3), and the bins were then placed on top of the plates (PICTURE 4). Drying was carried out in a large hall so the sludge was in contact with the open air, as can be seen from PICTURE 4. During the outside drying, temperatures were 0-10°C, dropping below 0°C during the night every now and then. It was also rainy and very moist most of the time.

These experiments relate closely to future development, i.e. if waste is to be processed, it has to be dried first, otherwise it becomes sticky. Drying it using large ovens takes up a lot of energy, so these experiments are to examine how these substances dry and if it is possible to dry them using floor heating, which would conserve energy and the environment. Floor heating can be problematic in the Finnish environment, where a typical year is mostly cold and also moist every now and then. Even if the sludge is to be dried in rotary furnaces, it would still be useful to pre-dry the sludge beforehand.



PICTURE 2. Heatwork HW1800 Thermal power station



PICTURE 3. Hot oil tubes under the aluminium plates.



PICTURE 4. Containers on top of the aluminium plates.

The compounds used in the experiments were compound residue, which is mostly jarosite, and zinc ferrite. Zinc ferrite is a leaching residue leftover from the process in the 1970s, when neutral acid leaching was applied, resulting in the forming of zinc ferrite. A small amount of it has been stored and fed into the roasting process. Zinc ferrite is however still made in some other smelters. Jarosite, on the other hand comes from leaching, during the process iron precipitates as jarosite, and is then removed from the main process (FIGURE 1). In the past, jarosite was filtered using a moving curtain filter, which resulted in 40% humidity. In the present day it is filtered using a pressure filter, which results in <30% humidity.

The experiments were started at the beginning of October 2020, the initial goal of the experiments having been to get the compound residue to 10% humidity. The compound residue was taken from two different places, outside banks and bins. The humidity at the beginning was 20% for the bin and 14% for the bank. There were 8 containers, half of which were from the bin and half from the outside bank. One half was kept static the entire time and half mixed every now and then. From both mixed and static containers one was 35 cm thick and the other one 50 cm thick.

Samples were taken from each of the bins every two hours and took them to the laboratory and measured the humidity by weighing the samples before and after they were in the oven for a couple of hours. Samples were gathered almost every weekday. At first the heating was turned off for the night, but when it was noticed that there was almost no drying taking place, the heating was left on for the night. After the first week the heating was also turned off for the weekend, but when the drying was still noticed to be slow, the heating was left on also for the weekend.

When it was noted that the compound residue was not drying with 50 cm thick layers (TABLE 1), the thickness of the layer was reduced to 20 cm. The experiments with compound residue were continued with 20 cm and 35 cm thick layers for about a week, after which the drying of the compound residue was started in the laboratory with a heating plate (TABLE 4), due to the sludge not drying in outdoor conditions. As the drying of compound residue was started in a laboratory, the drying of zinc ferrite was also started outdoors in the same manner compound residue was dried before in the tests.

The humidity of the zinc ferrite was about 30% at the beginning of the tests, when the goal was to achieve 10-14% humidity. After a week of constant heating the drying outdoors was ended for the zinc ferrite as well, as basically no drying was observed (TABLE 2), and moved to the laboratory (TABLE 3; FIGURE 9). At first the drying was conducted for a few hours at a time in 60°C and mixed using a spoon every 30 minutes, then the compound was sealed off with a diaphragm. The drying was far more successful in laboratory conditions, where the desired humidity was achieved for zinc ferrite in 19 hours.

TABLE 1. Humidity of the 50 cm thick layer of compound residue dried with the floor heating outside at 60°C

12.10	21%
13.10	21%
13.10	21.8%
14.10	21%
20.10	23.5%
21.10	24%
21.10	24.3%
22.10	23.3%

TABLE 2. Humidity of the 35 cm thick layer of zinc ferrite dried with the floor heating outside at 60°C

28.10	28%
29.10	28.7%
2.11	28.0%
3.11	27.1%
4.11	27.5%

TABLE 3. Drying results for zinc ferrite in a laboratory at 60°C

Time (h)	Humidity(%
0	32.9%
1	33.8 %
2	30%
1 2 3	30.9 %
4	30.3 %
5	29.6 %
6	27.5 %
7	26.7 %
8	27.3 %
10	24.2 %
11	21.5 %
12	23.0 %
13	22.1 %
14	20.3 %
15	17.8 %
16	17.2 %
17	14.8 %
18	13.4 %
19	12.7 %

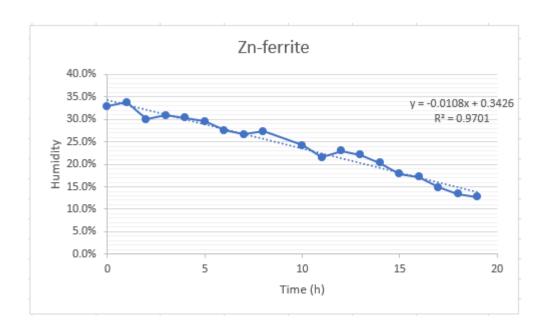


FIGURE 9. Graphical display of the humidity of zinc ferrite at 60°C

TABLE 4. Drying results for compound residue in a laboratory at 60°C

Time (h)	Humidity(%)
1	21.6%
2	20.7%
3	19.5%
4	19.8%
5	19.0%
6	17.7%
7	16.7%
8	17.5%
9	16.5%
10	13.9%
11	12.9%

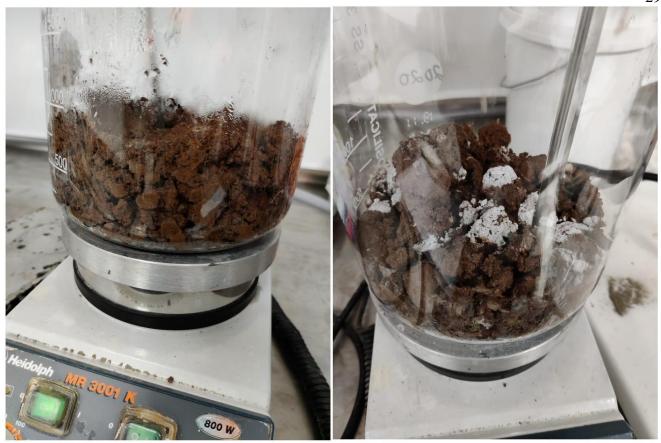
It was then decided to keep the drying constant for eight hours in different temperatures for both substances to see how much of a difference in humidity would a 10°C difference make. (TABLE 5; TABLE 6.) It was also noted that by the end of the eight-hour drying session the sludge at the bottom of the glass was very dry and powder-like and stuck to the bottom of the glass, while at the top the sludge retained its original shape. The humidity was calculated as an average value of the top, middle and bottom humidities.

TABLE 5. Drying results for an eight-hour constant drying session for compound residue in laboratory conditions

Start	26 %
70C	25.15%
80C	16.85%

TABLE 6. Drying results for eight-hour constant drying session for zinc ferrite in laboratory conditions.

Start	27.5%
60C	22.9%
70C	9.9%



PICTURE 5. Zinc ferrite before and after an eight hour drying session at 70°C

5 CONCLUSION

The experiments were conducted to see if drying would happen without the need to construct a large building for the drying process. Otherwise the sludge has to be dried in large ovens, so drying them using floor heating would conserve energy and the environment. Based on the results of the tests, at least a large hall is needed if floor heating is used for the drying of sludge. Drying outside generates too much waste heat and the surroundings is too humid and temperatures in Finland vary too much. The hall should have sufficient ventilation to blow humid air away so dry air can replace it, which can absorb more humidity from the sludges. It would also help the drying process if hot air could flow through and around the sludge.

As was noticed from the laboratory tests, drying is far more successful and faster in conditions where the temperature stays constant. There was also sufficient air ventilation in the laboratory. An optimal temperature for the floor heating should also be determined accurately, it cannot be too high or the concrete underneath will start to crack, but it also cannot be too low or the drying won't be efficient enough. For the zinc ferrite, a sufficient temperature would appear to be around 70°C as can be seen from Table 6, the drying can also be seen from the sludge itself in practice (PICTURE 5).

Possible waste heat from the zinc production process could be used to provide heat for the drying by, for example using an exit gas washer for the flue gases that come from the processes at Boliden Kokkola. District heating uses hot water circulating in large pipes to provide heat to customers, the water then returns to the plant in a cooler temperature. One possible solution to bring about the required energy for the drying could be to take advantage of this potential surplus heat in the returning water, which would also benefit the district heating plant by lowering the temperature of the returning water while also lowering the costs of decreasing the temperature of returning water.

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