Roni järvensivu

Reuse Possibilities for Elemental Sulfur Sludge

Helsinki Metropolia University of Applied Sciences

Bachelors Degree

Degree Programme in Environmental Engineering

Final Thesis

17.4.2015

Author(s) Title Number of Pages Date	Roni Järvensivu Reuse Possibilities for Elemental Sulfur Sludge 33 pages + 2 appendices 17 April 2015
Degree	Bachelor of Engineering
Degree Programme	Environmental Engineering
Specialisation option	Waste and Water Treatment Technology
Instructor(s)	Kaj Lindedahl, Lecturer, Metropolia AMK Sauli Kopalainen, Operational manager, HSY Christoph Gareis, Operational manager, HSY

Gas collected from the landfill for power generation at Ämmässuo contains hydrogen sulfide, a toxic gas formed from decomposing organic matter. Hydrogen sulfide will form sulfuric acid in the presence of water vapor and is thus corrosive and unwanted in gas treatment systems. In addition to wearing the motors and acidifying the oils used at the combined heat and power plant, combustion of sulfur-containing gasses will result in the formation of sulfur dioxide, a toxic and harmful pollutant.

In order to remove hydrogen sulfide from landfill gas, The Helsinki Region Environmental Services HSY decided to install a desulfurization plant manufactured by Paques. The installed THIOPAQ unit removes hydrogen sulfide from the raw gas without diluting it with air. Raw gas is washed counter-currently with a caustic fluid, which absorbs sulfide from the raw landfill gas. The sulfide is biologically converted into elemental sulfur, which is then discharged from the process as sludge.

The aim of this thesis project was to research different reuse possibilities for the elemental sulfur sludge formed during desulfurization. Options where elemental sulfur can be used as a raw material were studied including composting, fertilizer production, sulfuric acid production, sulfur containing concrete and sulfur enhanced asphalt mixtures. Research was conducted so that the restrictions and goals of Helsinki Region Environmental Services were kept in mind.

Research conducted provides Helsinki Region Environmental Services with an insight on possible reuse options. The results of this thesis work can be used as basis for deciding the best course of action for the effluent usage or disposal. Research shows that using the sludge as fertilizer would be one of the best methods for sulfur reuse, the same consensus is shared by the manufacturers of similar desulfurization units and Paques, but other options researched are equally promising.

Keywords	sulfur, desulfurization, HSY, THIOPAQ

Tekijä Otsikko Sivumäärä Aika	Roni Järvensivu Alkuaine rikki lietteen uusiokäyttö mahdollisuudet 33 sivua + 2 liitettä 17 huhtikuuta 2015
Tutkinto	Insinööri (AMK)
Koulutusohjelma	Ympäristötekniikan koulutusohjelma
Suuntautumisvaihtoehto	Jätteen ja veden käsittelytekniikat
Ohjaajat	Kaj Lindedahl, Lehtori, Metropolia AMK Sauli Kopalainen, Toimintovastaava, HSY Christoph Gareis, Toimintovastaava, HSY

Kaatopaikkakaasu, jota hyödynnetään energian tuotannossa, sisältää myrkyllistä rikkivetykaasua. Kaasua hyödynnettäessä rikkivety reagoi ilman kosteuden kanssa muodostaen syövyttävää rikkihappoa. Rikkihappo syövyttää voimalaitoksen laitteistoja ja happamoittaa öljyjä. Lisäksi rikkiä sisältävän kaasun polttaminen muodostaa ympäristölle haitallista rikkidioksidi kaasua.

Helsingin Seudun Ympäristöpalvelut -kuntayhtymä hankki rikkivety kaasun poistamista varten THIOPAQ rikinpoistolaitteen. Laitetta valmistaa Paques-niminen hollantilainen yritys. Kaatopaikkakaasusta poistetaan rikki laimentamatta kaasua. Lipeä liuos, jolla kaatopaikkakaasua pestään, imee itseensä kaasusta sulfidin. Bakteerit muuntavat biologisesti sulfidin alkuaine rikiksi, joka poistetaan rikinpoistolaitteesta lietemäisessä muodossa.

Tämän lopputyön tavoitteena oli tutkia eri käyttömahdollisuuksia rikinpoistolaitoksessa muodostuvalle alkuaine rikkilietteelle. Työssä tutkittiin erityisesti rikkilietteen käyttöä kompostoinnissa, lannoitteena, rikkihapon valmistuksessa, betonin raaka-aineena ja asfaltin valmistuksessa. Tehtiin tutkimusta Helsingin Seudun Ympäristöpalveluiden näkökulmasta, pitäen mielessä kunnallisen yrityksen rajoitteet ja tavoitteet.

Suoritettu tutkimus antaa Helsingin Seudun Ympäristöpalveluille pohjatietoa lietteen käyttömahdollisuuksista. Työn tuloksia on mahdollista käyttää pohjustuksena lietteen käyttötarkoituksen suunnittelussa. Yksikään tutkituista aiheista ei ollut muita selvästi parempi vaihtoehto, mutta lannoitteena käytöstä on eniten kokemusta ja suosituksia niin rikinpoistolaitteen valmistajalta, kuin myös muiden vastaavanlaisien poistolaitteiden valmistajilta.

Avainsanat	Rikki, Rikinpoistolaite, HSY, THIOPAQ

Contents

Abbreviations

CHP	Combined Heat and Power
HSY	Helsinki Region Environmental Services
YTV	Pääkaupunkiseudun yhteistyövaltuuskunta
ORC	Organic Rankine Cycle
VOC	Volatile Organic Compounds
LC50	Lethal concentration, 50%
VYL	Finnish Association of Landscape Industries
TSS	Total Suspended Solids
SCU	Sulfur Coated Urea
GTK	Geological survey of Finland
WSA	Wet sulfuric acid process

1 Introduction

Hydrogen sulfide is a toxic, corrosive and flammable gas present in the raw biogas collected from the landfill site at Ämmässuo Waste Treatment Center. Hydrogen sulfide forms when organic matter decomposes in an anaerobic process. Hydrogen sulfide is often also present in natural and volcanic gasses. Landfill gas is used to generate power at a combined heat and power (in short CHP) plant at Ämmässuo. In order to minimize the wear of the generators and to minimize the sulfur dioxide emissions from the power plant a desulfurization plant was installed.

THIOPAQ desulfurization plant washes landfill gas with alkaline water and bacteria converts the hydrogen sulfide into elementary sulfur. The sulfur from this process is extracted from the desulfurization plant as a sludge mainly consisting of elementary sulfur, but also containing small amounts of thiosulfate, sulfate, sodium and carbonate. The purpose of this thesis was to study different environmentally friendly options for reuse of the formed sludge.

This thesis project was commissioned in late autumn 2014 by Helsinki Region Environmental Services. The project was done in order to get better knowledge on possibilities for environmentally conscious and economically feasible ways of disposing the formed effluents. Paques the manufacturer of the desulfurization plant has stated that they are willing to transport the formed sulfur and treat it elsewhere if it is first dried. As the mission of Helsinki Region Environmental Services is to promote environmental awareness it is advisable to follow the company's policies and as such try to find an environmentally friendly way of reusing the effluent. The aim of this thesis project is to find the most ecological and feasible way to reuse the effluents formed. Theory and knowledge acquired in this thesis project is used as a basis for deciding the actions done for the reuse or final disposal of sulfur sludge.

2 Helsinki Region Environmental Services

2.1 Organization

Helsinki Region Environmental Services in short HSY is responsible for the clean drinking water for over a million citizens in the capital region. In addition to providing safe potable water, it is in charge of waste and wastewater processing, air-quality monitoring and providing environmental information for the citizens and businesses of the metropolitan area. It is the leading promoter of ecological living and tries its best to achieve its goals while keeping the environmental issues in mind. HSY started its operations in 2010 when the water treatment facilities of Espoo, Helsinki, Kauniainen, Vantaa and the waste treatment facilities of Pääkaupunkiseudun yhteistyövaltuuskunta in short YTV joined to form a large merger. HSY employs around 750 professionals in the metropolitan area. /1/

2.2 Ämmässuo

Ämmässuo Waste Treatment Center treats biodegradable waste, contaminated soils, wood waste, fly ash, bottom ash and mixed municipal waste. The treatment center covers a land area of 200 hectares at the border of the cities Espoo and Kirkkonummi. Ämmässuo is the only operational landfill area in the capital city region. During 2014 Ämmässuo treatment facility received 328 266 tons of waste and soil material. Of the received amount only 76 000 tons of waste was landfilled, rest of the material was used in composting, structural building of the landfill, treated and stored for later use or sent to the waste incineration plant after sorting at the treatment center./2/

Landfilling of biodegradable and other organic waste is restricted from the beginning of 2016 by the Finnish directive on landfilling 331/2013. The strategy and processes at Ämmässuo are changing. By the end of 2014, the treatment of mixed waste started at Vantaa Energy’s waste incineration plant meaning that the traffic to the treatment center slowed down and most of the landfilling activities had ceased. Comparing 2013 and 2014 amount of landfilled material there was 64% less material landfilled, due to the incineration of mixed waste. Remaining activities at the treatment center are collection and treatment of landfill gas, treatment of biodegradable waste, collection of waste from nearby inhabitants, treatment of fly ash, bottom ash and clinker from the incineration plant, treatment of contaminated soils, gypsum treatment and landfilling of inorganic waste. /2, 3/

With the ending landfilling activities, there are new opportunities to be taken at Ämmässuo. The vision of HSY for the future of Ämmässuo treatment center is to have a resource-efficient and material recycling cluster of industrial activities operating at the area. The ecological industrial center offers new and existing companies great IT-networks, an existing road network, a reliable green energy source with plans for further expanding the renewable energy production, possibilities for co-operation and extensive land area for testing and developing new processes. /4/

2.2.1 Landfill gas

Landfill gas is biogas formed when organic matter breaks down anaerobically inside the compacted landfilling area. The gas collected from the Ämmässuo landfill mostly consists of methane (CH_4), carbon dioxide (CO_2), water vapour (H_2O) and hydrogen sulfide (H_2S) gas. The content of the landfill gas is described in the mass balance sheet provided by Paques in appendix 1. Pretreatment of the gas before power generation is advisable for most efficient power generation and to ensure the longevity of the generator and motors of the combined heat and power plant.

During 2014 in total 47.23 million nm^3 of landfill gas was collected at Ämmässuo. Of the collected gas 12% was flared. The utilization degree of gas was 88% in 2014, which corresponds to about 198 GWh of energy. The amount of electricity generated in 2014, was 88.98 GWh and 10.08 GWh of heat was collected from the power generators cooling water. The collected heat was used for heating all the facilities at Ämmässuo. /2/

The CHP plant in Ämmässuo started its operations in May 2010 and is one of the largest landfill gas utilizing power plants in Europe. The combustion plant has 4 gas motors and an Organic Rankine Cycle (ORC) process which can produce energy from the combustion plants flue gasses. Landfill gas is collected from both of the landfilling areas. /5/

2.2.2 Treatment of biowaste

HSY collects biowaste in the capital city region and treats it in the Ämmässuo waste-treatment facility. Annually the facility receives roughly 50 000 tons of source-separated biowaste. In addition to municipal biowaste, the treatment facility receives and treats industrial biowaste and garden waste from the capital region. The facility received 36

000 tons of municipal biowaste, 13 000 tons of industrial biowaste and 12 700 tons of gardening waste in 2014. /2 /

The biowaste treatment facility consists of two composting facilities, first one so called “old composting plant” started its operation in 1998 and the newer plant, referred to as “composting plant” started operation in 2007. The composting plant consists of a receiving hall where the biowaste is collected, pretreatment equipment which sieves impurities from the incoming material and the composting tunnels. Biowaste is mixed with bulky agent to attain a mixture where sufficient air can pass the material. The composting plant has 15 tunnels of which the last 7 are so called hygienization tunnels where the material is kept at over 60°C for two consecutive days in order to eliminate pathogenic bacteria present in the organic waste. The old composting plant consists of 9 tunnels where the hygienizised biowaste from the composting plant is treated to mature the compost more before treating it out on the composting fields.

Biowaste is treated both in the two facilities and on the composting field in windrows. The municipal and industrial biowaste is pretreated and hygienized in the new and old composting plants, the garden waste is straight treated in windrows on the field. Biowaste is treated for approximately 2 weeks at the composting plant and then further 2 weeks at the old composting plant before the material is mature enough for field treatment where the material matures for several months. The composting windrows are mechanically turned every three weeks to get the material aerated. The temperature of the compost is monitored throughout the field maturing period. The garden waste compost needs to be at over 55°C for two consecutive weeks for it to be considered hygienizised.

2.2.3 Other landfill activities

Ämmässuo recycling station opened for operation in 2002. This station accepts several different kinds of waste for a fee depending on the type of waste and weight of the cargo. Accepted waste grades are metal waste, electrical and electronic waste, mixed waste, garden waste, cooling units, treated wood, twigs and branches, energy waste and dangerous waste. In 2014, Ämmässuo recycling station served in total 39 500 customers. /2/

A large hall for treating contaminated soils is located at Ämmässuo. The hall is covering a land area of 5000 m^2 and is equipped with exhaust air systems. The contaminated soils are mechanically aerated in the hall by wheel loaders. In 2014, no soils containing volatile organic compounds (VOC) were treated in the hall, so the installed VOC exhaust air system was not in use. Part of the contaminated soil hall was used for storing gypsum board waste. All together 11 340 tons of contaminated soils were received in 2014, of which 789 tons were classified as dangerously contaminated waste. /2/

Beginning of 2014 Ämmässuo started receiving both bottom- and fly ash, from here on referred as ash and clinker, from the new waste-to-energy plant in Vantaa. An experimental stabilizing process for the ash started immediately in April of 2014 and the experimental treatment of clinker in the fall of 2014. Ash is stabilized with cement and water to form a dense substance; 4067 tons of the stabilized cement was formed to be disposed of. After the startup of the waste-to-energy plant 42 049 tons of clinker was transported to Ämmässuo. From the received amount, roughly 32 500 tons of clinker was treated. Clinker is aged in large piles and treated in 20 000 to 30 000 ton batches. Metals are separated from the clinker, 2500 tons of magnetic metals and 1800 tons of non-magnetic metals were separated from the treated clinker. Separated metals were sold to metal processing companies for production of secondary raw materials. /2/

Gypsum mainly collected at the recycling stations is transported to Ämmässuo and stored in the contaminated soils treatment hall. The stored gypsum boards are treated when the amount reaches 1 300 tons. This happens usually every 1 to 2 years. When the desired mass of waste is reached, a special mobile gypsum treatment device is transported to the treatment facility to separate the gypsum from impurities. During 2014, roughly 913 tons of gypsum waste was transported to Ämmässuo treatment facility. /2/

3 Methodology

This thesis is based on literature research, training provided by the manufacturer of the desulfurization plant and on knowledge and information gathered during working at the biodegradable waste treatment facility in Ämmässuo. Different ways for using elemental sulfur as a raw material were researched. The research done focused on processes and methods that could be applied at Ämmässuo. Theoretical knowledge of the desulfurization plants operation and process description was gained through manuals provided by the manufacturer and participation in training provided at the treatment center.

Laboratory experiments conducted at Ämmässuo in autumn 2014 are used as background theory on the applicability of sulfur in soil amendment material produced from compost. The experimentation carried out determined an optimum mixture ratio for biodegradable waste, sand and peat in order to reach a stable pH of 7. The experiment and in addition monthly surveillance analyses conducted on maturing compost is used to determine if there is a need for adding sulfur to the raw compost according to the Finnish Association of Landscape Industries.

After the desulfurization unit's process startup, during stable operation, a sample of the process water was taken. The sample was taken from the sulfur pump into a 1 liter plastic bottle. The sample was sent to MetropoliLab for further analyzing of the process water's contents.

4 Sulfur

Sulfur can be found in its elemental form on the earth's surface. It is present as a yellow solid powder or crystal in room temperature, and can be mined from underground deposits. Sulfur has a melting point of 119°C, and its boiling point is 445°C. It is highly reactive and is a strong reducing agent; occurring reactions are usually exothermic. Sulfur is the world's 13th most abundant element. The most common way of acquiring sulfur is through desulfurization of sour gas and refining oil. /6, 7/

The sulfur cycle in the environment is similar to that of nitrogen. The sulfur cycle is presented in figure 1. Sulfur is released by the decomposition of organic matter in the soil. Bacteria oxidize the sulfur into sulfate which is readily available for plants to uptake. Sulfur is removed from the cycle by leaching and by harvesting crops. Sulfur is added to the soil by means of precipitation of sulfate containing rain and through fertilizers and soil amendments. Sulfate is a negatively charged ion and is soluble in water therefore; it is mobile in the soil structure. It is prone to leaching unlike the insoluble elemental sulfur. Soils that are often sulfur deficient are coarse textured and do not have organic matter as a source of sulfur. /8, 9/

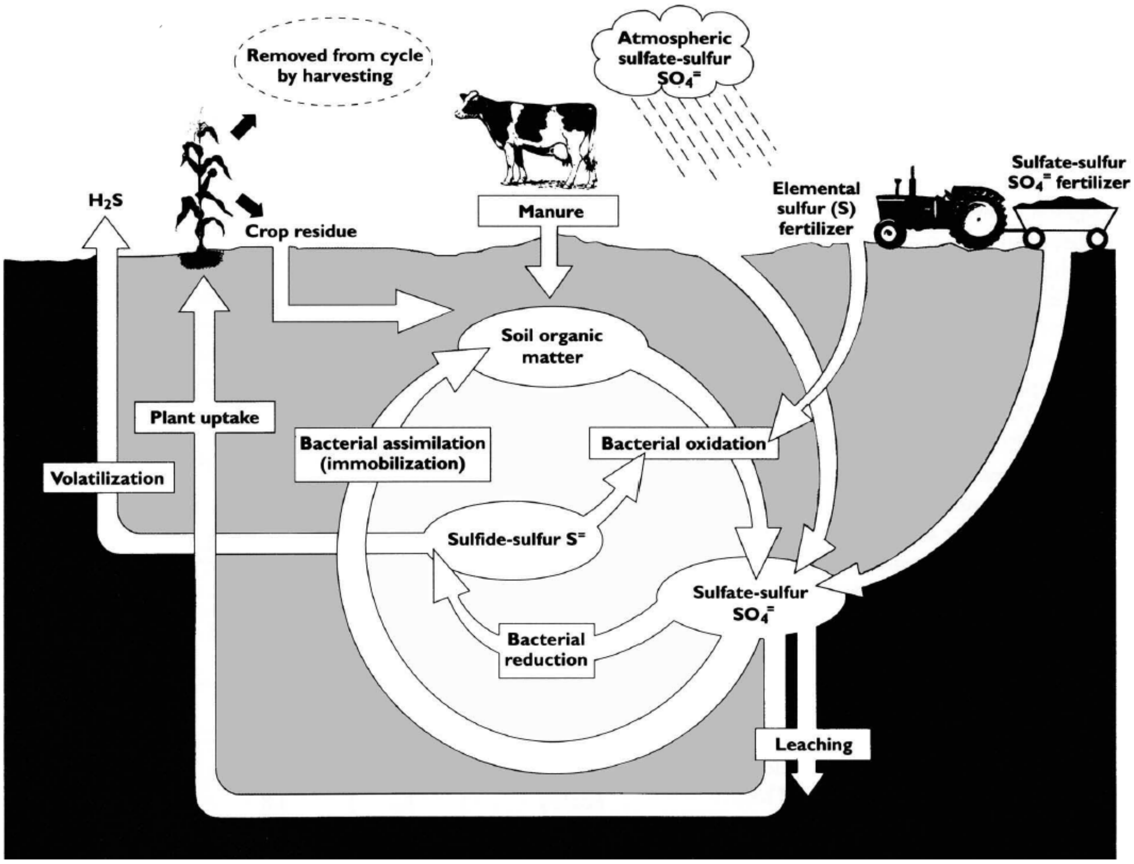

Figure 1 Sulfur cycle /8/

Sulfur belongs to the secondary nutrient category, but it is almost as important as the three main nutrients nitrogen, potassium and phosphate. Sulfur is important in the formation of several proteins and activation of enzymes in a plant. It is needed in the formation of cysteine, cystine (L-Cysteine disulfide) and methionine amino acids found both in animals and plants. Plants that suffer from sulfur deficiency might have thin stems and may seem pale. The new leaves of the plant are thin and pale unlike with nitrogen deficiency which appears first on older leaves of the plant. /8, 9/

Sulfur forms several different compounds and one of them is hydrogen sulfide, which is often present in natural gasses. Hydrogen sulfide forms when organic matter decomposes in anaerobic conditions. Bacteria reduce sulfates using the oxygen as an energy source and as such excreting hydrogen sulfide as a waste. It is one of the main reasons for landfill gas desulfurization at Ämmässuo. Hydrogen sulfide is a mild acid when dissolved in water and as such is problematic for gas processing where moist gas is to be processed. The hydrogen sulfide and moisture corrode the equipment used for gas processing. Hydrogen sulfide at concentrations of 800 ppm and exposure of 5 minutes is lethal for 50% of humans (LC50). /7/

Combustion of sulfur forms sulfur dioxide, which is a toxic gas with an irritating rotten smell. Sulfur dioxide is an intermediate step in the production of sulfuric acid. It can also be used as a food preservative and in the European Union it is marked as E220 in food labeling. Sulfur dioxide is also an important part in wine production. It is present in the wine and acts as an antibiotic and antioxidant preventing spoilage of wine. Sulfur dioxide emissions from different combustion units are regulated in order to limit the formation of acidic precipitate. /7, 10/

Solid sulfur should be stored separate from ignition sources and dust formation of sulfur should be avoided. Sulfur dust has a risk of explosion. Storing is advised to happen in cool, dry and sealed containers. Often sulfur is stored in liquid form for less risk of dust formation and easier pumping from one container to another. For transportation of sulfur, each container should be labeled according to regulations. Each container should contain UN 1350 or UN 2448 which are labels for sulfur. /7/

5 THIOPAQ desulfurization plant

5.1 Paques

Paques was founded in 1960 by Johan Pãques selling equipment for farmers in the Netherlands. In the early days of the company the focus was on constructing storage silos for farmers. During the energy crisis the focus and business sector of the company shifted to energy and environmental development. The company sold its first manure fermentation plant in 1978 and soon after in 1983 Paques was already fully committed to anaerobic water treatment processes. During the 90’s the company added newly invented sulfur technologies to its arsenal. /11/

5.2 THIOPAQ

THIOPAQ desulfurization process is safe and efficient in removing hydrogen sulfide from raw gas streams. *Thio* originates from the Greek language and can be translated as sulfur. It is widely used by the chemical industry as a prefix for sulfur-containing compounds. Hydrogen sulfide-containing gas is washed through a packed column bed counter-current to a caustic stream. The caustic strips the hydrogen sulfide from the incoming sour gas and releases the gas virtually free of sulfur from the exhaust pipe. The absorbed hydrogen sulfide is transformed into elemental sulfur by the biological activities in the system. THIOPAQ desulfurization system is especially favorable when the possibilities for effluent treatment are slim or nonexistent, since the formed effluent is rather stable on its own and most of the time does not need further treatment. The system is designed for treatment of gas in close to ambient conditions in temperatures ranging from 30°C to 40°C and close to normal ambient pressures. For more demanding gas there is a variant of the THIOPAQ system (Shell-Paques) that can process low-, medium- and high-pressure gasses with additional components installed. /12, 13/

The THIOPAQ system has been proven effective at over 120 operational installations worldwide. The system is notably reliable with uptimes close to 98% of the time and the ability to treat gasses with fluctuating concentrations of sulfur. The operational manager of the landfill gas power plant Sauli Kopalainen stated that one of the reasons for selecting the THIOPAQ system over competing systems is the ability to treat biogas without diluting it with air. /14/

5.3 Thiobacillus

Thiobacillus bacteria are responsible for the oxidation of sulfide into elemental sulfur in the desulfurization plants process. The bioreactor contains several different strains of genus Thiobacillus. Thiobacillus microbe is a naturally occurring usually thermophilic and acidophilic bacteria. Thiobacillus is common in mine wastes where it can oxidize pyrites, sulfurs and sulfur compounds. The oxidation can lead to problems, since commonly acids are formed, but the bacteria are also used efficiently in extraction of valuable metals. The strains present in the THIOPAQ desulfurization plant are exceptional as they are mesophilic and prefer conditions closer to neutral pH. Thiobacillus break down the sulfide only requiring oxygen as a source of energy. In order for the bacteria to grow in the bioreactor, additional nutrients are supplied for the Thiobacillus. A special Nutrimix provided by Paques is used. Under normal operation of the process approximately 30 ml of the Nutrimix is automatically dosed for every kilogram of sulfur removed from the system. /15, 16, 17/

5.4 Process description

Sour landfill gas enters the washer from the bottom of the washing column, the sour gas travels through a packed column bed where it contacts with the lean alkaline washing fluid. The column is packed with plastic filling material in order to achieve the maximal surface area for the liquid and gas to come into contact. The washing fluid reacts with the gas absorbing the hydrogen sulfide from the landfill gas into the fluid acidifying the fluid at the same time. The washing liquid moves from the bottom of the washer into the bioreactor due to gravitational pull, the two containers are interconnected. In the bioreactor biological processes convert the sulfide rich fluid mainly into elemental sulfur. The sulfur is pumped with the recirculation pump into a settling area where it slowly settles to the bottom of the settler and then is pumped out of the container as a sulfur containing sludge. The process scheme can be found from figure 2. /16, 12/

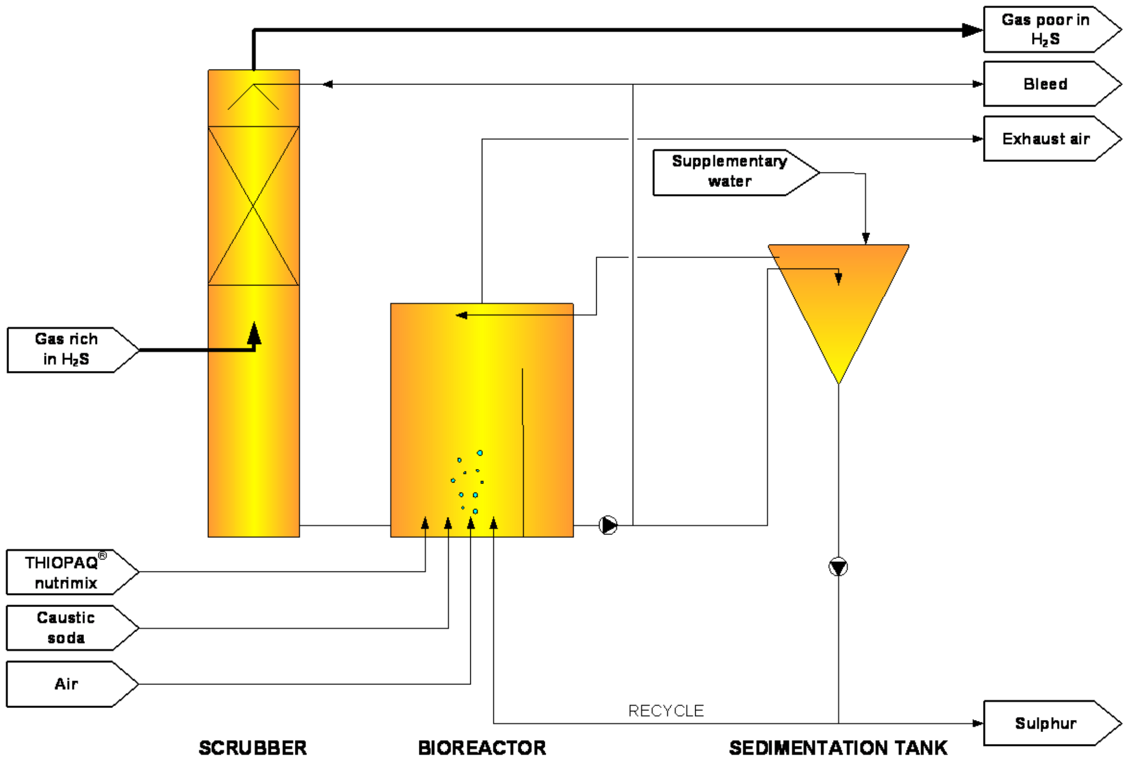

Figure 2 Thiopaq desulfurization plant process scheme /16/

5.4.1 Scrubber

Incoming gas is absorbed by the lean caustic fluid (sodium hydroxide NaOH). Hydrogen sulfide and carbon dioxide move from gas phase to liquid phase in the absorbing process. The pH of the lean washing solution decreases but the level is sustained by controlling the alkalinity of the washing fluid. The buffering ability (alkalinity) is determined from the amount of CO_2 in the influent. Alkalinity of the fluid can be controlled with addition of caustic soda into the system. Alkalinity affects the ability of the process to absorb H_2S from the gas, higher alkalinity means better absorption. /16, 18/

Reactions from gas to liquid phase in the scrubber are as follows:

$H_2S + NaOH \rightarrow NaHS + H_2O$ Hydrogen sulfide stripping in the scrubber.

$CO_2 + OH^- \rightarrow HCO_3^-$ Carbon dioxide stripping in the scrubber.

In the liquid phase of the scrubber, the incoming lean solution is transformed into the sulfur rich solution with the absorption of sulfide and carbon dioxide from the gas phase.

The sulfide concentration in the lean solution is very low, meaning that there is a significant difference in the concentrations between the gas and liquid phase allowing high removal of H_2S from the gas phase. Absorption of the gas allows for reduction of carbonate in the alkaline washing fluid and the neutralization of hydroxide ions, additionally polysulfide is formed as a side reaction in the scrubber. /16, 18/

Lean to rich fluid solution reactions

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$	Bicarbonate formation in the scrubber.
$H^+ + OH^- \rightarrow H_2O$	Neutralization of hydroxide ions.
$xS + HS^- \rightarrow S_xS^{2-} + H^+$	Polysulfide formation in the scrubber.

5.4.2 Bioreactor

Scrubber and bioreactor are interconnected and the sump part of the scrubber acts as an airlock between the two vessels. The airlock is necessary in order to prevent gas from entering the bioreactor. Sulfide and polysulfide are biologically converted into elemental sulfur in the bioreactor in the presence of oxygen. Bicarbonate formed in the scrubber is oxidized back into carbonate in the bioreactor and the caustic is regenerated, thus forming the lean alkaline solution which is recirculated back into the scrubber.

Sulfide oxidizing bacteria (Thiobacillus) are present in the process fluid of the bioreactor. The conversion of sulfide to elemental sulfur is controlled by the amount of available oxygen in the reactor. High sulfide to oxygen ratio is favorable for the maximum conversion to elemental sulfur. If the process is leaning to more oxygen available than sulfide, the biomass will oxidize the sulfide and sulfur present in the reactor into unwanted sulfate and sometimes even sulfuric acid. These side reactions are undesirable since extra caustic soda is needed for neutralizing the formed acid. Oxygen is pumped through nozzles distributed evenly throughout the reactor allowing for an even distribution of oxygen for the biomass. /16, 18/

Biological reactions in the bioreactor

$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$	Biological process for carbonate formation.
$NaHS + \frac{1}{2}O_2 \rightarrow S + NaOH$	Biological process for sulfur conversion.

Biological side reactions in the bioreactor

$HS^- + 2\ O_2 + OH^- \rightarrow SO_4^{2-} + H_2O$	Sulfate oxidation in the bioreactor.
$S + 2\ OH^- + \frac{3}{2}O_2 \rightarrow SO_4^{2-} + H_2O$	Sulfur oxidation into sulfate.
$S_xS^{2-} + O_2 \rightarrow (x+1)S + O_2$	Biological conversion of polysulfide into sulfur.

Chemical side reactions will take place in the reactor if sulfide concentrations are allowed to rise too high. Thiosulfate and polysulfides are formed if the system is not functioning desirably. The formation occurs if there is a reduction in biological oxidation or if the sulfide concentration is very high compared to the amount of available oxygen. The formation of polysulfides can be easily recognized from the green color of the lean/rich alkaline solution in the system. /16, 18/

Chemical side reaction

$2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O$	Thiosulfate formation in the bioreactor.
$xS + HS^- \rightarrow S_xS^{2-} + H^+$	Polysulfide formation in the bioreactor.

5.4.3 Process water recirculation pump

A process water recirculation pump circulates lean solution from the bioreactor to several different locations in the system. The main flow for the lean solution is the lean solution spraying in the scrubber, without this the inflowing gas would not be washed with the caustic solution. Part of the flow is circulated for spraying the solution from below the gas inlet in the scrubber and from the top of the bioreactor to stop foam formation. In addition, the lean solution is circulated through the measuring loop where pH, temperature and redox potential are measured. The recirculation pump has part of the stream directed to the sulfur settler and for lean solution bleeding out of the system to ensure that not too much sulfate is built up in the system. /16/

5.4.4 Sedimentation tank

The bioreactor has a part of its container separated from the normal aerated reactor area. This area is the sedimentation tank where sulfur is separated from the lean solution. The settling of biomass and sulfur controls the total suspended solids (TSS) concentration of the bioreactor. TSS in the bioreactor is between 5-25 g/l and in the settler the concentration increases to 50-250 g/l. /18/

Sulfur and biomass settle from the lean solution by gravitation. The concentrated sludge is then circulated back into the bioreactor or discharged from the system. Circulation back into the bioreactor occurs when the TSS concentration in the bioreactor is too low. Pumping much TSS out of the system will lead to a situation where the process fluid level is too low and extra make-up water needs to be added into the process. Lean solution with low TSS concentration flows back into the bioreactor. /18/

5.5 Effluents formed

THIOPAQ desulfurization plant has three effluent streams, the cleaned gas stream, the bleed stream and the sulfur sludge flow. Excess air is vented out of the bioreactor. Air leaving the bioreactor has normally very low concentrations of hydrogen sulfide, around 1 ppm. In special situations the hydrogen sulfide concentration may rise up to 10-15 ppm but these situations are exceptional and brief. The amount of bleed formed from the system depends on the state of the process. If the process functions idealistically, the amount of bleed is very minimal, almost negligible. Sulfur containing sludge is pumped from the system with steady intervals approximately 200 liters per hour. The theoretical mass balance of the system containing the sludge production can be found from appendix 1. /18/

5.5.1 Sulfur sludge sample

A sample of the sulfur sludge was taken on the 12th of March 2015 from the sulfur sludge discharge pump. The sulfur sludge was sent to MetropoliLab in Helsinki for analyses. The sample was analyzed for elemental sulfur, sulfate, thiosulfate, carbonate, bicarbonate, carbon dioxide and sodium concentrations and in addition for alkalinity. The results only represent the condition of the desulfurization plant at that point of time. Due to the sample being lost before all of the ordered analyses could be completed, some of the needed results are missing. Analysis results can be found in Appendix 2.

6 Process monitoring

In order to manage the correct functioning of the desulfurization plant, the make-up water, lean and rich solutions and the incoming raw gas need to be monitored. Daily and weekly analyses of the solutions are to be made and documented. The desulfurization plant is equipped with sampling points for both liquid and gaseous samples.

For liquid samples, there is a sampling tap located in the sensor loop and a sulfur sludge outlet after the sludge pump. Gas samples are collected from two different points in the scrubber, one for raw gas and one for lean gas. Sampling points for the gas need to be fitted with elastic fittings that make the sampling with Dräger tubes air tight.

6.1 Sampling and Analysis timetable

Paques has provided a model schedule for the sampling and analyses to be conducted at the desulfurization plant when it is completely operational and running at a steady state. Schedule for the sampling can be found from table 1. During the startup phase sampling frequency has to be increased in order to follow the process start up properly. The analyzing schedule has been made to help keep the process running at its optimum; thus, it is advisable to follow the given schedule. The process state has to be regularly checked in order to keep the system operating as intended.

Table 1 Paques analysing timetable /18/

Analysis	Frequency (analyses per week)				Method
	Make-up water	Bio-reactor	Gas in	Gas out	
pH	-	5	-	-	Standard
Conductivity	-	5	-	-	Standard
Alkalinity	-	5	-	-	Paques
Color	-	5	-	-	Paques
Sulfide (HS^-)	-	Incidental	-	-	Standard
Sulfate (SO_4^{2-})	-	Incidental	-	-	Standard
Thiosulfate ($S_2O_3^{2-}$)	-	Incidental	-	-	Standard
Water hardness	Incidental	Incidental	-	-	Standard
Magnesium (Mg^{2+})	Incidental	Incidental	-	-	Standard
Sulfide (H_2S)	-	-	5	5	Dräger tubes
Carbon dioxide	-	-	1/month	1/month	Dräger tubes
TSS	-	1	-	-	Paques
Solids (Imhoff)	-	5	-	-	Paques

Normal parameters of the system pH, conductivity, alkalinity, color and the concentration of solids in the bioreactor need to be monitored 5 times a week corresponding to once per normal working day. Parameters that are less likely to change have more lax sampling cycles.

6.2 Analyses to be conducted

6.2.1 PH & conductivity

The pH and conductivity of the reactor make-up water is to be analyzed with a common laboratory pH and conductivity measuring probe. Sample is to be taken from the sampling point and transported into a laboratory where 250 ml – 500 ml of the make-up water is to be inserted into a beaker. The calibrated conductivity sensor is placed in the beaker from where it reads the value in mS/cm. The same sample can be used for measuring the pH of the sample. /18/

6.2.2 Alkalinity

Alkalinity of the water expresses the ability of a solution to resist change in pH. It can be determined with a simple titration with hydrochloric acid. The amount of acid needed to bring the solution to a pH of 4.0 indicates the alkalinity of the sample.

Make-up water is to be filtered and close to 100 ml of the filtered sample is to be placed in a 250 ml beaker. The beaker is to be filled to the 100 ml mark with demineralized water. A pH electrode is to be placed in the beaker for measuring the change occurring. Hydrochloric acid with a molarity of 0.1 is titrated in to the sample until the pH reaches 4.0, and then the alkalinity of make-up water is calculated simply by dividing the volume of titrated hydrochloric acid by the volume of the filtered sample and multiplying by 0.1. This gives the alkalinity of the sample in mol/l. /18/

$$\frac{V_{HCl}}{V_{titrated\ sample}} \times 0{,}1 = Alkalinity$$

6.2.3 Color of the solution

Color of the process fluid is a simple way of determining if the process is healthy. The color of the process fluid can be observed from a see through vessel in the sensor loop. Normal color for the lean process fluid is whitish yellow and when the process is not functioning well, the color might change. When the process is polysulfide-rich the process fluid turns green. /16/

6.2.4 Dräger tubes

The sulfide and carbon dioxide concentrations in the biogas can be easily measured with Dräger tubes. The Dräger tube is placed inside a cleaned pump and pumped for a specific amount of times corresponding to the concentration range of the tube. Concentration of the measured particle is read from the side of the tube, where a scale indicates the concentration of the observed pollutant.

6.2.5 Total Suspended Solids

Weekly a sample from the make-up water is collected. The sample is used for determining the total suspended solids concentration in the bioreactor. A known volume of the make-up water is filtered through an ash-free filter. Weight of the filter and a crucible are weighed before the experiment. The filter including the suspended solids is dried on a crucible overnight in a drying oven. The dried sample is weighed, and the results are documented. The total suspended solids concentration can be calculated by dividing the mass of the solids left on the filter after drying with the known original volume of the sample. Using the equation below the total suspended solids can be calculated, and the result is presented in grams per liter (g/l). /18/

$$TSS = \frac{M_{crucible+filter+dry\ sample} - M_{crucible} - M_{filter}}{V_{sample}}$$

6.2.6 Concentration of solids (Imhoff)

In order to determine the concentration of solids in the reactor make-up water, a sample is taken daily. An Imhoff funnel is filled with the sample process fluid up to the 1000 ml mark, the process fluid is left to settle for an hour. After the solids from the fluid have settled in the funnel, volume of the settled sludge can be determined from the scale on the side of the Imhoff funnel. During the start-up of the system a calibration curve should be made. Both Imhoff measurement and TSS should be repeated for 10 consecutive days, and the values should be plotted to form a calibration curve. If the TSS and Imhoff relation differs more than 25% during normal operation, a new calibration graph should be made. /18/

7 Sulfur sludge reuse possibilities

7.1 Use in composting

Biodegradable waste from the metropolitan area is composted at a biodegradable waste treatment plant at Ämmässuo, as such adding sulfur sludge from the desulfurization plant to the formed compost would be straightforward and easy to implement. The compost formed at the biodegradable waste treatment facility is used in production of soil improvement agent. Sulfur is an important nutrient for plant growth. It acts as a catalyst in chlorophyll production, so insufficient amounts will affect the overall growth of plants. Plants can only uptake specific amounts of sulfur and the rest is left in the underlying soil. Excessive sulfur is not toxic or poisonous for the crops, but can lead to lowering pH of the soil which may not be desirable. Lower pH level decreases the intake of sulfur, so having more than the needed amount of sulfur can lead to actually less sulfur being conveyed to the plant. Excessive sulfur is lost from the soil by leaching and is then carried to surrounding waterways where it can lead to further problems.

As sulfur is an important nutrient in soils the possibility of adding it to the produced compost at Ämmässuo was studied. The guide lines for seedbeds produced by the Finnish Association of Landscape Industries (VYL) and the analytical information stored of prior compost produced at the biodegradable waste treatment facility were used to determine the usefulness of additional sulfur in the compost. Compost is mixed with sand and peat to form a mixture suitable for a wide variety of crops.

The recommended amount of sulfur for yard soils, grass areas and for modest plants is 20-30 mg/l and the suggested upper limit is 200 mg/l. During soil mixture experiments done in September 2014, the optimal ratio of sand, compost and peat in small scale was determined. The experiments showed that the optimal pH of 7 can be achieved with a mixture with 60% sand, 25% compost and 15% peat of the volume. Sulfur concentrations in the sand can be neglected. According to a study made by the Geological Survey of Finland (GTK) in 2009 the average content of sulfur in peat was 0,24% of the dry weight. Even if the sulfur present in peat is neglected, the sulfur content of the soil is 1/4th of the sulfur amount in the compost. /19, 20/

Analyzing results of compost that has been sold for soil improving agent production was obtained from the biodegradable waste treatment plants internal records. Partial records from 2011 to present day were accessible and sulfur concentrations analyzed at Novallabs and MetropoliLab were stored in the archives. An average of 2259 mg/l sulfur concentration can be calculated from compost treated at the biodegradable waste treatment plant. Garden waste composted on the fields had an average of 588 mg/l concentration of sulfur. High concentrations of sulfur in the biodegradable waste compost show that there is no need for additional sulfur in the end product. Adding sulfur to the product in order to lower the pH might be useful for achieving desired pH levels. Sludge from the desulfurization plant also contains carbonate which can be useful for compost in providing additional carbon to the end product and also stabilizing the product.

7.2 Use as a fertilizer

The most widely used applications for elementary sulfur are production of sulfuric acid and use in fertilizing. The sulfur can be used straight in production of different fertilizers, or first turned into sulfuric acid which then can be mixed to form a more suitable fertilizer for the crop. Fertilizers can be divided into two primary categories depending on which state the sulfur is in. First the more commonly used sulfate fertilizers where the sulfur is in sulfate form and readily available for crops to intake and the second type elemental sulfur fertilizers where the sulfur is present in its elemental form. The elemental sulfur needs to be oxidized into sulfate before plants are able to uptake it as a nutrient. Small particle size and warm conditions greatly enhance the oxidation rate of elemental sulfur.

Common sulfur containing fertilizers are ammonium sulfate, ammonium thiosulfate, superphosphate, potassium sulfate and calcium sulfate more commonly known as gypsum. Ammonium sulfate and gypsum can be acquired as byproducts from other industrial activities. Ammonium sulfate is a byproduct extracted from coke ovens and gypsum is formed during production of phosphate fertilizers. Ammonium thiosulfate is produced by reacting sulfur dioxide with ammonia forming ammonium sulfite, which is then reacted with elemental sulfur to form the ammonium thiosulfate. Potassium sulfate and superphosphate can be manufactured using sulfuric acid. Potassium sulfate is manufactured by reacting potassium chloride and sulfuric acid forming the potassium sulfate and hydrochloric acid. Superphosphate is manufactured by reacting sulfuric acid with phosphate rock. /21, 22/

Elemental sulfur can be used as a fertilizer in several different ways, such as sulfur coated urea, sulfur bentonites and on its own. Sulfur coated urea from here on SCU is manufactured by coating hot urea with molten sulfur and sealing it with polyethylene or microcrystalline wax. SCU is a controlled-release fertilizer allowing for slow and precise release of the nutrients in to the soil. Advantage of the controlled-release fertilizer is that the fertilizer resists leaching, it does not need bacteria to convert the nutrients into an oxidized state, and it offers slower release rate than conventional sulfate based fertilizers. Downside of SCU is the high production costs limiting the usage so far to horticulture and small patch landscaping. Sulfur bentonite can be used as a fertilizer and also as a soil amendment product. It can be used to lower the pH of alkaline soils. The bentonite is a small pastille like product which contains large amounts of small sulfur particles. Bentonite contains special swelling agents for easily expanding the small pastille to cover a larger contact area. It resists leaching until the sulfur is oxidized into sulfate. Small sulfur particle size greatly shortens the conversion time needed for sulfur to be oxidized into sulfate, and at the same time larger particles are left waiting for the next season. /23, 24/

Sulfur can be used on its own as a fertilizer amending the possible sulfur deficiency problems that soils may have. Using dry powdery sulfur is not advisable as it contains a risk of explosion. Sulfur mixed in water in the form of sludge or slurry is advised to be used. The very fine particle size of sulfur formed from the THIOPAQ desulfurization plant is ideal for use as a fertilizer. In addition to having a small particle size which helps in the oxidation of sulfur into sulfate, the effluent sludge from the THIOPAQ process contains sodium salts, sulfate and carbonate, which are all useful nutrients. /25/

7.3 Sulfuric acid production

Sulfuric acid production is the most widely used output for sulfur. Large part of the produced sulfuric acid is used in fertilizer production, but it is also the most widely used chemical in the world. The most used process for sulfuric acid production is the manufacturing of phosphoric acid, which is a key ingredient in phosphate fertilizer production. It is used in several different chemical and manufacturing processes. Sulfuric acid is produced by oxidizing sulfur dioxide SO_2 into sulfur trioxide SO_3. The sulfur trioxide is then reacted to form sulfuric acid H_2SO_4. /6, 26, 27/

Sulfuric acid can be manufactured from several different sulfur sources such as elemental sulfur, sulfide ores, regenerating spent sulfuric acid or combusting hydrogen sulfide containing gasses. There are several methods for sulfuric acid manufacturing, but the most common method is the conventional contact process. Wet gas sulfuric acid (WSA) process is also a noteworthy method since it can be used to produce sulfuric acid from almost all sulfur containing gasses.

In the contact process, SO_3 is absorbed into sulfuric acid forming oleum $H_2S_2O_7$ which is then diluted with water to form sulfuric acid. Direct mixing of sulfur trioxide with water is avoided due to the highly exothermic nature of the reaction. In the wet process SO_3 is hydrated forming sulfuric acid gas, which is then finally condensed into liquid sulfuric acid.

In the contact process, forming sulfuric acid from elemental sulfur is carried out by oxidizing the solid sulfur into SO_2 gas by burning the sulfur at 900-1000°C in a single- or two-stage combustion unit in the presence of oxygen. The formed SO_2 gas is then further reacted to form SO_3. /27/

$$\mathrm{SO_2} + \frac{1}{2}\mathrm{O_2} \xleftrightarrow{\mathrm{V_2O_5}} \mathrm{SO_3} \Delta\mathrm{H} = -99\mathrm{kj\ mol^{-1}}$$ Formation of sulfur trioxide.

Sulfur trioxide is formed in the presence of a catalyst, commonly vanadium pentoxide. The process is exothermic; therefore, the waste heat is collected and the formed gas is cooled. Recovered heat is recycled for other processes. Sulfur trioxide is then absorbed into concentrated sulfuric acid (98.3 – 98.7%) to form oleum. The fluid used for absorbing sulfur trioxide is around 70°C to 120°C. Water is added to the fluid breaking the formed oleum into sulfuric acid and at the same time maintaining the appropriate sulfuric acid concentration for the continuation of the absorbing of sulfur trioxide. /27/

Producing sulfuric acid from hydrogen sulfide containing gasses with the WSA process is effective and can be applied for gasses with low to high H_2S concentrations. Gasses with lower than 25% H_2S content may need supplementary fuel for the incineration of the gas. In the wet sulfuric acid process, sulfur containing gasses are combusted to form SO_2 the formed SO_2 is oxidized into SO_3 in the presence of catalysts usually vanadium pentoxide. Hydration of SO_3 happens when the moist air and SO_3 react to form sulfuric acid in gas form. The gaseous sulfuric acid is then condensed into liquid form. /28/

7.4 Sulfur enhanced asphalt

Sulfur enhanced asphalt has been used in the 70's and 80's during the oil embargo. Bitumen, a side product of the petroleum industry was hard to obtain as a raw material and sulfur has been abundant and practical raw material to use as a replacement of bitumen. During the oil crisis hot molten sulfur was mixed and used to replace part of the bitumen in the asphalt. Even though early attempts in sulfur enhanced asphalt showed positive improvements in the asphalt properties, formed H_2S during the manufacturing of the asphalt was a large concern. With the growing environmental consciousness and stricter emission directives desulfurization has become even more common and sulfur as a raw material even more abundant. New interest in using sulfur as a construction material has led to development of sulfur enhanced asphalt with more desirable properties than standard asphalt. /29/

Sulfur can be added to conventional warm asphalt mixing plants. The optimal mixing temperature for the sulfur enhanced asphalt mixture is 135°C, beyond 150°C the formation of H_2S is increased. Sulfur Enhanced asphalt mixtures are mixed at temperatures up to 20°C lower than conventional hot asphalt mixing; this means that less CO_2 is formed and might also lead to lower costs. Sulfur asphalt mixing plants should be equipped with H_2S detecting gas meters with the alarm level being 10 ppm. /30, 31/

Thiopave sulfur enhanced asphalt product patented by Shell. It is a sulfur asphalt mixture with 25% of the bitumen being replaced by elemental sulfur. The sulfur is added as solid pellets, which melt in the hot mixture to form the binder. Wax is added to the mixture to allow for better handling of the produced mixture. Other studies suggest that mixtures of 30% sulfur and 70% asphalt show good results. The upper limit of positive results for sulfur in the binder is 40%. Studies conducted in Saudi Arabia using elemental sulfur in pellet form showed that the sulfur enhanced asphalt mixture has better rut resistance, higher stiffness and better tensile strength. Studies conducted on the Shell Thiopave by the National center for asphalt technology in the United States show that the sulfur enhanced asphalt is stiffer than conventional asphalt, has a higher cycle to failure rate and the Thiopave containing mixture showed improved fatigue performance measured by beam fatigue testing. /30, 31, 32/

7.5 Concrete sulfur

Mixtures of sulfur and sand were already reported in the 1920’s showing that the material had exceptional acid resistance and excellent strength. It was also noted that the material lost its flexural strength when subdued to temperature changes. In the 1970’s interest in using sulfur as a construction material grew due to the abundance of sulfur as a raw material. Interest both in the United States and Canada led to research and development of methods for using sulfur as a construction material. The joint research created the modern corrosion-resistant sulfur concrete. /29/

Modified sulfur is mixed with aggregate to form a concrete with desirable properties such as excellent corrosion resistance, good freeze-thaw resistance, low permeability and very fast curing time of 24 hours. Early sulfur concrete attempts were made by mixing liquid elemental sulfur with aggregate, these mixtures showed problems with temperature cycling. This can be explained with the properties of sulfur as a material. The unmodified sulfur decreases in volume when cooled down creating large tension in the material and additional stress to the material will cause it to break down. Including different polymers will result in an end product with exceptional strength, corrosion and freeze-thaw resistance, fast curing times and ability to recycle the product. /33/

Production of sulfur concrete is resembles asphalt production. Sulfur and other components of the mixture are heated to 140-150°C where they are mixed to form the sulfur concrete. Higher temperatures will result in the formation of SO_2 gas. The molten sulfur concrete can be poured into a precast mold or used as pour-in-place cement. /33/

Sulfurcrete developed by Dr. Alan Vroom in the early 1970’s is a patented sulfur concrete technology using a proprietary polymer modifier SRX™ produced by Cominco. Sulfurcrete is a widely used product with good corrosion resistance, high strength, low permeability and fast setting times. A typical mixture ratio for Sulfurcrete can be found from table 2. /34/

Table 2 Composition of Sulfurcrete by weight percent /34/

Component	Weight percent
SRX^{tm} Sulfur Modifier	1,2
Sulfur	11,5
Coarse Aggregate	42
Fine Aggregate	40
Mineral Filler	5,3

Sulfurcrete is used in industrial applications where exceptional corrosion resistance is needed, such as fertilizer storage containers, and it is especially good in marine conditions where conventional portland cement is susceptible to corrosion. In addition to industrial applications where corrosion resistance is needed, the sulfurcrete can be applied for use in bricks, paving stones, sewer pipe and other construction elements. Sulfur concrete should not be used in applications where high heat is required, since sulfur is a thermoplastic element. The sulfur would start melting above its melting of 119°C, meaning that the material would lose its structural integrity. /33/

8 Future advancements on the matter

Results from MetropoliLab were late and missing part of the results due to the laboratory misplacing the sample before all analyses could be completed. Analyzes that were completed on time and reported on show results that differ from daily analyzing conducted by a representative from Sarlin, who is responsible for the commissioning phase of the desulfurization plant. The results obtained found from Appendix 2, show that the sample would only contain 3 g/l sulfur even though internal analyses showed 10-15 g/l depending on the day. A possible explanation for the inconsistencies in results could be caused by not properly mixing the sludge before conducting the experiments. As sulfur is not very water soluble it forms sediments in the bottom of the container rapidly. If the sample is not properly mixed the part sample could possibly be representing the top part of the container with much smaller concentrations of sulfur. Sending new samples to two different laboratories and comparing results from both of the laboratories would result in more trustworthy results.

Deciding on a possible dewatering or concentration unit for the sludge treatment is next on the agenda. Using the sludge as a fertilizer would mean that the product shouldn't be completely dried, as it is much easier to store and spread as a liquid fertilizer product than as a solid powder. In addition for being easier to spread, the common problem of explosion risks associated with the powdery sulfur is avoided. The sludge contains sulfates which are readily available for the nutrients and also elemental sulfur, which would later in the cycle oxidize into sulfate available for the consumption of the crops. /25/

If the sludge is decided to be completely dried, several options for the usage are opened. Purity of the dried elemental sulfur should be analyzed. The dry solid sulfur could be marketed for production of sulfuric acid, asphalt binder, concrete binder and for several different smaller industrial applications such as vulcanization of rubber.

8.1.1 Sludge dewatering or concentration and wastewater

The TSS concentration inside the bioreactor is between 5 and 25 g/l, and the biomass is concentrated in the settler to 50 – 250 g/l. The sludge leaving the desulfurization plant is still relatively low in solid content, and it should be concentrated or dewatered for optimal storage and transportation. Concentrating and dewatering the sludge creates a situation where wastewater needing treatment is created. Circulation of the wastewater back into

the bioreactor as make-up water is possible, resulting in only small amounts of bleed being discharged into the wastewater sewage system. /16, 18/
Dewatering the sulfur sludge with a press, decanter centrifuge or belt thickener can result in having sulfur sludge with more than 50% dry solids content and 95 - 98% sulfur purity, this can be used directly as fertilizer or sold as is. For better purity, the sludge can be diluted again and run through a second dewatering for extracting dissolved salts from the sulfur getting sulfur sludge with close to 99% purity. Drying after the concentration leads to a solid powder. /25/

If for some reason the effluent from sludge dewatering is not recirculated to the bioreactor, the wastewater should be treated. Effluent from the desulfurization plant may contain up to 30 g/l of sulfate. Meaning that in the worst case scenario, wastewater containing up to 30g/l of sulfate would need to be discharged. A considered option for disposal of the wastewater would be to recirculate it through the landfill. The sulfate limits for disposing at the landfill is 20 g/l and the limit for problem waste landfilling is 30 g/l. Depending on the healthiness of the system and on how much of the sulfate is collected with the elemental sulfur, the water could be circulated through the normal landfill operation.

9 Conclusions on the different options for sulfur usage

9.1.1 Impact on the environment

Selling the formed sulfur sludge for production of sulfuric acid is the only option studied that does not have a clear environmentally positive aspect. It does not have any distinctive feature that separates it from any other sulfur source, since most of the sulfur used for sulfuric acid production is from different gas or process cleaning installations. Producing sulfur enhanced asphalt requires less energy than conventional asphalt due to the lower temperature needed for the sulfur handling. Concrete with sulfur as a binder can be recycled by crushing the material and heating it above its melting point for re-pouring. Using sulfur for production of fertilizer returns the sulfur back in to the cycle and provides nutritive impact on farmed crops. Studies conducted by Alberta Agricultural Research Institute show that there is a gain in crop yield after fertilization with sulfur paste from the Thiopaq desulfurization plant. The use of sulfur in compost would have a similar effect as using it as a fertilizer. The most environmentally friendly use for the formed sulfur would be to use it locally at Ämmässuo. Longer transportation means more emissions formed. /25/

9.1.2 Sulfur in garden waste compost

Mixing the sulfur sludge with garden waste in order to lower the pH of the compost and to attain slightly more desirable nutrient values is something to seriously take into consideration. Completion of the anaerobic digestion plant for biowaste treatment will considerably change the quality of biodegradable waste compost produced at Ämmässuo. Current use of the garden and biodegradable waste compost is selling the material to Kekkilä for production of soil improving agents. The future plan of HSY is to transform its approach of selling compost into producing and selling soil improving agents, but the current plan only concerns the compost produced from biowaste. At the time of writing this thesis the future of garden waste compost is still undecided. One approach would be to use it as a bulky agent in the anaerobic digestion or in the final composting of the digestate. This would then mean that the extra sulfur would be transferred into the digestion where it is unwanted.

9.1.3 Concrete and asphalt production at Ämmässuo

Sulfur enhanced concrete and asphalt production, could be a feasible end of life disposal option for the formed sulfur. Using elemental sulfur in concrete or asphalt production would mean that the sludge should be dried and depending on the use purpose maybe pelletized for better handling of the mixtures. HSY is interested in having a company specializing in asphalt or concrete products in its new eco industrial area. HSY could offer both stabilized ash from the waste incineration plant and sulfur as concrete binder for the companies.

9.1.4 Fertilizer production

Use of the sulfur as a fertilizer is something Paques recommends for the formed sulfur sludge and several studies show good results in crop yield with sulfur based fertilizers. Producing fertilizer as a product HSY would sell seems like a decent idea to approach. HSY would need to apply for a permit for selling the fertilizer, and as it is owned by municipalities it is not allowed to make profit with the selling of the product. An interesting topic needing more research is producing a fertilizer from a mixture of the treated gypsum and the sulfur formed. Both of the materials are used as fertilizers on their own and as such could possibly be a product with useful nutritive impact. Selling the dried elemental sulfur for production of phosphate based fertilizers is a feasible solution for the disposal of formed sulfur.

9.1.5 Sulfuric acid

Production of sulfuric acid at the Ämmässuo is not an option; the amount of elemental sulfur produced is so small in quantity that the operation of a sulfuric acid manufacturing plant is not economically possible. The best option would be to sell the raw dried elemental sulfur to a producer of sulfuric acid inside Finland. Several companies produce sulfuric acid from elemental sulfur in Finland. In addition a contract for selling the dilute sulfuric acid formed from the desulfurization unit, treating biogas from the anaerobic digestion plant could be included.

References

1. HSY. HSY työnantajana. [Internet]; 2015.[cited 1 January 2015]. Available from: https://www.hsy.fi/fi/hsytietoa/hsytyonantajana/Sivut/default.aspx

2. Kuisma-Granvik Sirkka, Uuksulainen J. Ämmässuon jätteenkäsittelykeskuksen toiminta vuonna 2014. 2015.

3. Finlex. *Valtioneuvoston asetus kaatopaikoista.* [Internet]; 2013.[cited 15 April 2015]. Avaiable from: http://www.finlex.fi/fi/laki/alkup/2013/20130331.

4. HSY. Ämmässuon Ekopuisto. [Internet]; 2015.[cited 15 February 2015]. Available from: https://www.hsy.fi/fi/asiantuntijalle/jatehuolto/jatteenkasittelykeskus/ekomo/Sivut/default.aspx

5. HSY. Kaatopaikkakaasun keräys. [Internet]; 2015.[cited 10 January 2015]. Available from: *https://www.hsy.fi/fi/asiantuntijalle/jatehuolto/jatteenkasittelykeskus/kaatopaikkakaasu/Sivut/default.aspx*

6. Sulfur institute. An Introduction to Sulfur. [Internet]; 2015.[cited 11 February 2015]. Available from: http://www.sulfurinstitute.org/learnmore/sulfur101.cfm

7. Työterveyslaitos. OVA-ohje:Rikki. [Internet]; 2014.[cited 24 February 2015]. Available from: http://www.ttl.fi/ova/rikki.html

8. E.E. Schulte and K.A. Kelling. Soil and Applied Sulfur. [Internet]; [cited 2 April 2015]. Available from: *http://www.soils.wisc.edu/extension/pubs/A2525.pdf*

9. Ray E. Lamond. Sulphur in Kansas. [Internet]; [cited 16 April 2015]. Available from: *http://www.ksre.ksu.edu/bookstore/pubs/MF2264.pdf*

10. Elintarviketurvallisuusvirasto. Rikkidioksidi. [Internet]; 2015.[cited 17 April 2015]. Available from: http://www.evira.fi/portal/fi/elintarvikkeet/tietoa+elintarvikkeista/koostumus/elintarvikeparanteet/lisaaineet/e-koodit/?a=showEcode&ecodeId=1856&itemsPerPage=5000

11. Paques. Paques Europe. [Internet]; 2015.[cited 11 January 2015]. Available from: http://en.paques.nl/about-us/subpages/paques-europe

12. Greenhouse Gas Technology Center Southern Research Institute. Test and Quality assurance plant. [Inetrnet]; 2004.[cited 12 December 2014]. Available from: *http://www.epa.gov/etv/pubs/600etv06028.pdf*

13. Dictionary.com. Thio-. [Internet]; 2015.[cited 17 April 2015]. Available from: http://dictionary.reference.com/browse/thio

14. Paques. Paques THIOPAQ. [Internet]; 2015.[cited 20 October 2014]. Available from: http://en.paques.nl/products/featured/THIOPAQ

15. Microbe wiki. Thiobacillus. [Internet]; 2015.[cited 15 January 2015]. Available from: https://microbewiki.kenyon.edu/index.php/Thiobacillus

16. Paques MVI. Operation & Maintenance manual THIOPAQ Type C. 2013.

17. Wobby Bosma, Paques. Thiopaq training course presentaition. 2015.

18. Paques MVI. Appendix B Operating procedures of Operating & Maintenance manual. 2013.

19. Viherympäristöliitto. Viherympäristöliiton suositukset kasvualustaohjearvoiksi. [Internet]; 2009.[cited 12 February 2015]. Available from: http://www.vyl.fi/userData/vyl/pdf/1258565162_Kasvualustaarvot.pdf

20. Teuvo Herranen, Geologian tutkimus keskus. Turpeen rikkipitoisuus Suomessa. 2009.

21. National Iranian Gas Company. Dry fertilizers containing sulfur. [Internet]; 2015.[cited 15 April 2015]. Available from: *http://sulfur.nigc.ir/en/sulfuruses/agri-cultural/sulfurfertilizers/drysulfatefertilizers*

22. National Iranian Gas Company. Fluid sulfur Fertilizer. [Internet]; 2015.[cited 16 April 2015]. Available from: *http://sulfur.nigc.ir/en/sulfuruses/agricultural/sulfurf-ertilizers/fluidfertilizerscontainingsulfate*

23. National Iranian Gas Company. Sulfur bentonite. [Internet]; 2015.[cited 17 April 2015]. Available from: http://sulfur.nigc.ir/en/sulfuruses/agricultural/sulfurfertiliz-ers/elementalsulfurfertilizers/sulfurbentonite

24. National Iranian Gas Company. Sulfur coated urea. [Internet]; 2015.[cited 17 April 2015]. Available from: http://sulfur.nigc.ir/en/sulfuruses/agricultural/sulfurf-ertilizers/elementalsulfurfertilizers/sulfurcoatedurea

25. Cameron Cline, Alie Hoksberg, Ray Abry and Albert Janssen. Biological process for H_2S removal from gas streams the SHELL-PAQUES/THIOPAQ gas desulfurization process. [Internet]; 2003.[cited 17 April 2015]. Available from: http://www.environmental-expert.com/Files%5C587%5Carti-cles%5C5529%5Cpaques6.pdf

26. Sulfur institute. Glossary. [Internet]; 2015.[cited 6 January 2015]. Available from: http://www.sulfurinstitute.org/learnmore/glossary.cfm

27. Ashar N.G. & Golwalkar K.R., Springer. A Practical Guide to the Manufacture of Sulfuric Acid, Oleums, and Sulfonating Agents. 2013.

28. Jens K. Laursen and Frans E. Jensen. Meeting industry demands. [Internet]; 2007.[cited 17 April 2015].Available from: http://www.topsoe.com/sites/default/files/topsoe_wsa_meet_industry_demands.ashx__3.pdf

29. W.C. McBee, T.A. Sullivan and H.L. Fike. Sulfur construction materials. [Internet]; 1985.[cited 16 January 2015]. Available from: http://digicoll.manoa.hawaii.edu/techreports/PDF/USBM-678.pdf

30. National Center for Asphalt Technology, Auburn University. Shell Thiopave test sections at pavement test track. [Internet]; 2010.[cited 17 April 2015]. Available from: http://www.ncat.us/files/research-synopses/shell-thiopave.pdf

31. National Center for Asphalt Technology, Auburn University. *Evaluation of mixture performance and structural capacity of pavements utilizing shell Thiopave.* [Internet]; 2010.[cited 16 April 2015]. Available from: http://www.ncat.us/files/reports/2009/rep09-05.pdf

32. Mohammed Al-Mehthel et.al., Saudi Aramco. Sulfur extended asphalt as a major outlet for sulfur. [Internet]; 2010.[cited 14 April 2015]. Available from: http://sulphurinstitute.org/pub/a03b8cac-d39b-e0e4-e48e-7e6cc11e995c

33. Natalia Ciak, Jolanta Harasymiuk. Sulfur concrete's technology and its application to the building industry. [Internet]; 2013.[cited 24 January 2015]. Available from: http://www.uwm.edu.pl/wnt/technicalsc/tech_16_4/ciak.pdf

34. H.A. Howard Okumura, Cominco. Sulfurcrete Sulfur Concrete Technology. [Internet];.[cited 12 January 2015]. Available from: http://www.sulphurinstitute.org/pub/a03beacb-aea4-7241-ac2c-cf23139cc5d7

Appendix 1. Paques mass balance table

PAQUES

Design Note

Project number : 2108284
Project name : Sarlin - Thiopaq 30/2 Landfill Helsinki
Subject : Mass Balance

Date : 24 september 2014
Author : Erik van Zessen
Approved by :

Vapor streams				
PFD stream name	Feed Gas	Treated Feed gas	Air in	Air out
PFD stream number	01	02	401	402
Pressure bara	1,20	1,10	1,00	1,00
Temperature C	40,00	40,36	20,00	40,30
Flow rate kmol/hr	245,54	246,90	7,93	11,19
Flow rate ton/year	57381,09	57016,91	1987,14	3037,90
Composition kg/hr				
H2S	5,84	0,41		<1e-4
CO2	3932,50	3823,13		107,28
NH3	0,00	0,000		0,00
C1	1932,86	1928,31		4,54
C2	0,00	0,00		0,00
C3	0,00	0,00		0,00
C4	0,00	0,00		0,00
H2	0,00	0,00		0,00
c6	0,00	0,00		0,00
N2	0,00	0,00	171,69	171,69
Other	458,17	458,17		
H2O	220,98	298,76	3,15	14,88
O2	NA	NA	52,00	48,40

Liquid streams					
PFD stream name	Bleed	Cake	Nutrients	Make-up water	Caustic 20 w%
PFD stream number	19	20	03	08	04
Pressure bara	atm	atm	ambient	ambient	ambient
Temperature C	40,30	40,30	ambient	ambient	ambient
pH	8,00	8,00	3,00	6-9	>12
Flow rate ton/year	0,00	703,88	1,41	1252,35	143,20
Composition kg/hr					
Total H2S	0,00	0,00			
Sodium Na	0,00	1,88			1,88
Carbondioxide CO2	0,00	0,02			
Bicarbonate HCO3	0,00	2,73			
Carbonate CO3	0,00	0,10			
Sulphate SO4	0,00	1,53			
Thiosulphate S2O3	0,00	0,09			
Elemental sulfur	0,00	4,55			

Reference DES013570_EN- (2108284) 24-09-2014 Page 1 of 1

Appendix 2. MetropoliLab process fluid analysis results

MetropoliLab TESTAUSSELOSTE 2015-4813 1(1)
17.04.2015

Tilaaja
2274241-9
HSY Jätehuolto, biojätteen käsittely

21464
Järvensivu Roni

PL 100
00066 HSY

Maksaja
HSY Helsingin seudun ympäristöpalvelut -kuntayhtymä
Ostolaskut

PL 303
00066 HSY

Näytetiedot

Näyte	Liete		
Näyte otettu	12.03.2015	**Kellonaika**	
Vastaanotettu	13.03.2015	**Kellonaika**	12.20
Tutkimus alkoi	13.03.2015	**Näytteenoton syy**	Tilaustutkimus
Näytteen ottaja	Tilaajan toimesta		

Analyysi		Menetelmä	4813-1 Liete S-liete, 12.3.2015	Yksikkö	Epävarmuus-%
Hiilidioksidi	*	SFS 3005:1981	6,7	mg/l	15
Sulfaatti, SO4	*	Sis.menet. DA	8 300	mg/l	10
Natrium, Na, kokonais	*	SFS-EN ISO 11885:2009	24 000	mg/l	20
Rikki, S, kokonais	*	SFS-EN ISO 11885:2009	3 100 000	µg/l	20

*=näyte tutkittu akkreditoidulla menetelmällä

Yhteyshenkilö Abenet Suzana, 010 3913 420, Kemisti

Kalso Seija
toimitusjohtaja

Tiedoksi Järvensivu Roni, roni.jarvensivu@hsy.fi

Akkreditointi ei koske lausuntoa. Analyysitulokset pätevät ainoastaan analysoiduille näytteille.
Analyysitodistuksen saa kopioida vain kokonaan. Muussa tapauksessa kopioinnista on saatava lupa.

Postiosoite Viikinkaari 4 00790 Helsinki metropolilab@metropolilab.fi http://www.metropolilab.fi
Puhelin +358 10 391 350
Faksi +358 9 310 31626
Y-tunnus 2340056-8
Alv. Nro FI23400568