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SCHOOL OF TECHNOLOGY AND INNOVATIONS

ENERGY TECHNOLOGY ENGINEERING

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DIFFERENT THERMAL ENERGY STORAGE TECHNOLOGIES

Master's thesis for the degree of Master of Science in Technology

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CONVERSIONS AND ABBREVIATIONS

SHS sensible heat storage

LTES latent thermal energy storage

CHS chemical heat storage & sorption

UGS underground gas storage

PHS pumped hydro storage

CAES compressed air energy storage

FES flywheel energy storage

TES thermal energy storage

TCHS thermo-chemical heat storage

HTF heat transfer fluid

COP coefficient of performance

BTES borehole thermal energy storage

DHE downhole heat exchanger

ATES aquifer thermal energy storage

HDPE high-density polyethylene

HWTES hot water thermal energy store

GWTES gravel-water thermal energy store

CHP combined heat and power

HVAC heating, ventilation and air-conditioning

UPH underground pumped hydro storage

PCM phase change materials

HDPE high-density polyethylene

SBS styrene butadiene styrene

EG expanded graphite

PEDMA macroporous poly (ethylene dimethacrylate)

DALY disability adjusted life years

GHG greenhouse gas

SGCHPES scheme of solar-ground coupled heat pump with energy storage

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ABSTRACT:

This thesis analyses and discusses about renewable energy and storing those energies. Especially it analyses underground storage systems with solar heat. In addition, it discusses storing that energy for use in later times. These storages systems have four different way of storing energy. Those four storages are sensible heat storage (SHS), latent thermal energy storage (LTES), chemical heat storage (sorption) and mechanical storage. These systems are analyzed. Then in order to get better efficiency heat pump need. Thesis explains this pump, too. In the result section, a discuss about health benefit, economic facts and effects on greenhouse gas are made for these storage methods. At last, conclusions section describes good and bad things about these systems.

KEYWORDS: thermal storage, renewable energy

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TIIVISTELMÄ:

Tämä diplomityö analysoi ja kuvaa uusiutuvaa energia ja sen varastoimista. Eritysesti se analysoi aurinkolämpöä käyttäviä maanalaisiavarastojärjestelmiä. Tämän lisäksi se kuvaa energian varastoimista myöhempään käyttöön. Näillä varastojärjestelmillä on neljä erilaista tapaa energian varastointiin. Nämä neljä varastointi tyyppiä ovat lämpötilan muutoksen perustuvavarastointi, latentti lämpöenergian varastointi, kemiallinen lämpövarastointi (sorptiot) ja mekaaninen varastointi. Näitä järjestelmiä analysoidaan. Lämpöpumppua käytetään paremman tehokkuuden saavuttamiseen. Tämä diplomityö kertoo myös näistä pumpuista. Tulososiossa kerrotaan varastomenetelmien terveysvaikutuksista, taloudellisuudesta ja vaikutuksesta kasvihuonekaasuihin. Lopuksi näiden järjestelmien hyvät ja huonot puolet esitetään päätöososa.

AVAINSANAT: lämpövarasto, uusiutuva energia

1 INTRODUCTION

Energy is important in today's world. In current time, energy need has increased because of high-energy use and growing population. Until recent years, fossil fuels have fulfilled the people's energy needs but fossil fuels have big disadvantages, which has caused environmental damages. Some of these damages have created global warming, toxic particles in the air and water and ground pollution. Global warming makes the ice melting in the north and south poles. This creates other chain reactions such as raising sea level. Also fossil fuels reserves are declining which have caused price increase in the recent years. This has created alternative ways to get the energy demand fixed. In order to reduce pollution renewable energies are the best candidates (N. Giordano, C. Comina, G. Mandrone and A. Cagni. 2015).

Most common renewable energies are solar energy, wind energy, bio energy, geothermal energy, tidal energy and hydro energy. These energy sources have drawbacks. Some of the drawbacks are high starting cost, poor efficiency, need bigger space and limited time availability. These sources are usually available when the demand is low and it can be solve by energy storage methods. One of the common sources of renewable energy is solar energy. It is much lower cost to start and widely available. However, it will need better cost, better efficiency and reliable storage system. In order to have it available energy for all year around. In recent years many efficient techniques were developed in to storage systems (N. Giordano, C. Comina, G. Mandrone and A. Cagni. 2015).

Some of the storage systems that are available in modern time are sensible heat storage (SHS), latent thermal energy storage (LTES), chemical heat storage (sorption), pumped hydro storage (PHS), compressed air energy storage (CAES) and flywheel energy storage (FES). Pumped hydro storage (PHS), flywheel energy storage (FES) and compressed air energy storage (CAES) are mechanical energy storage system. Sensible heat storage (SHS), latent thermal energy storage (LTES) and chemical heat storage (sorption) are thermal energy storage system (TES). In this thesis generally those three types of TES: sensible heat storage (SHS), latent heat storage (LHS) and thermochemical heat storage (TCHS) or sorption were discuss. There storage systems are used

as a solar collector as the prime energy source. Also TES system uses heat pump in order to get better efficiency.

2 METHODOLOGY

2.1 Solar collector and heat transfer fluid (HTF)

Solar energy is one of most abundant renewable energy source available. According to L. Prasad and P. Muthukumar article the earth gets 3.8·10²³ kW of solar energy. In this energy approximately 1.8·10¹⁴ kW could be harvest as a renewable energy. Rests of the energies were reflect back to atmosphere. If we able to turned 0.1% of the this energy to electricity or heat energy with 10% efficiency it would be enough to feed more than four time globe energy (1.8·10¹⁰ kW) need. It is about 0.4·10¹⁰ kW of energy. In order to harvest solar thermal energy which is inexhaustible and it is available free. Solar collector is one of the good technique to cultivating the solar energy. In the recent years, the solar collector technology has been improving. The prices of components are dropping and can be produce in vast quantities. Also maintaining cost is reduces rapidly. Top of that this energy can be storage in ground and able to put in use all year long. According to N. Giordano and his term, the most common methods for storing the solar thermal energy are sensible heat storage (SHS) and latent thermal energy storage (LTES).

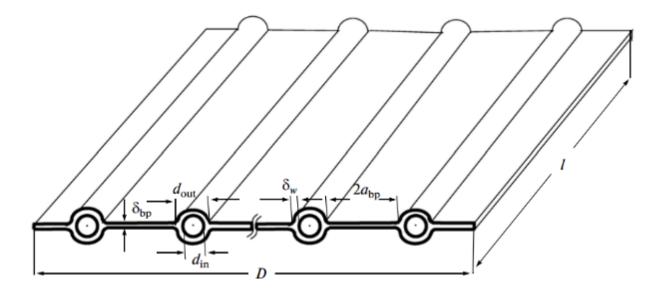


Figure 1. Solar collectors (N. R. Avezova, 2010)

As seen in Fig. 1 the sheet piped beam (which is between the recovering heat pipes) absorbing heat for the sun. Its width is shown $2a_{bp}$ (distance between recovering heat pipes) and its thickness is δ_{bp} . The inside recovering heat pipes collected the heat and bring to inside the building or heat pump. Its diameter is shown as d_{in} . The D and l are width and length of the whole solar panel. The fluid recovering the heat is heat transfer fluid (HTF). It is cooler when it got into the solar collector and it leaves with solar heat to the storage. These panels work as car's radiator but only different is doing opposite job.

Some of the heat transfer fluids are water, NaNO₃/KNO₃ mixture, water ethanol (glycol) mixture, galactitol (sugar alcohol), erythnitol, xylitol, D-mannitol, air, natriumacetat and magnesiumnitrat (G. John, A. Konig-Haagen, C.K. King-ondu, D. Bruggemann and L. Nkhonjera 2015). The temperature of the transfer fluids is critical. These fluids vary depending on the place. For instance, in the winter-summer weather countries have to use antifreeze heat transfer fluid because of freeze protection in the winter, spring and autumn. In addition, some of the other things play in rolls to choosing the right fluid. Those are price of the fluid, corrosion level of fluid, thickness of the fluid, made of the material, thickness of tubes which fluid runs, melting point of the fluid, environment concerns of the fluid and range of temperatures of the storage (R. Grena and P. Tarquini, 2011).

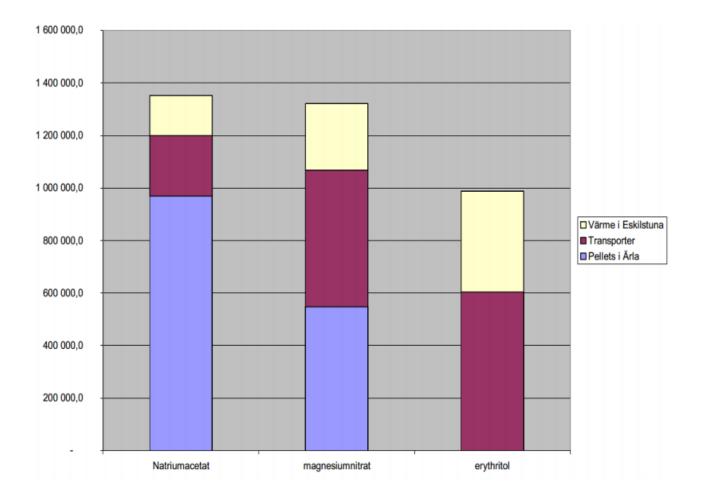


Figure 2. Annual cost for delivered heat depending on the choice of PCM (E. Milisic 2013)

As shown Fig. 2 clearly how erythritol (Sugar alcohol) is saving money when it is use as a heat transfer fluid (HTF) from solar collectors to heat storage tanks. The blue colour shows cost of delivering the energy. In addition, it can be able to use in freezing temperate and high melting temperature (shown in light yellow). For example, it can transport high temperature different and lower degradation. The lower degradation means it has high cycle (over 500 cycling) before it loss it is character. Other positive things with erythritol is its high latent heat of fusion, non-toxic nature, easy availability, large latent heat and its good operational safety (G.Kumaresan, R. Velraj and S.Iniyan 2011).

Also synthetic oils are good heat transfer fluids too but expensive and a hazard to environment makes them unpopular choice. Other hand water is one of the common use as heat transfer fluid because of water is inexpensive, easy to handle, non-toxic, noncombustible, high specific heat and widely available. If water is use as, heating fluid then there is no need to use heat exchangers because of it has high specific heat. The drawbacks of this heat transfer fluid is temperature limitation (might freeze or boil), high corrosive and difficult to stratify. Some cases air use as heat transfer fluid to storing heat (L. Socaciu 2012).

2.2 Heat pump

Table 1. The effect on your heating bills (Nordic heating & cooling, 2016)

	ELECTRIC BASEBOARD	AIR SOURCE HEAT PUMP	GEOTHERMAL HEAT PUMP
COP	1.00	2.92	3.89
Efficiency	100%	292%	389%
Yearly Electric Consumption	\$4,000	\$1,369	\$1,028

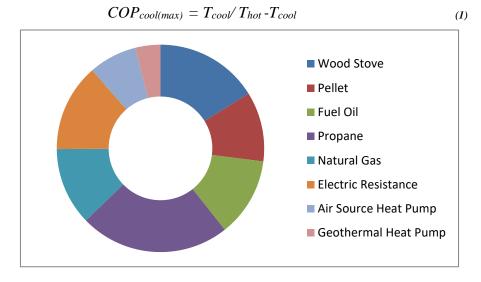
According to W. Wang and X. Zhang's article, the geothermal storage concept heat pump technology is one of the important systems in nowadays. It is usage in the storage category has growing a rate of 30% yearly. One of good thing about heat pump is that it can able to upgrade from low quality to high-quality energy. It makes a good candidate to change low heat solar energy to high heat energy. It has been in use for last 50 years but until now, it was use as space heating and air to air heating. The heat pump and renewal energy combination would be the ultimate way getting best efficiently for all year around. This system is expensive than conventional system but long term this is the best option.

As seen in Table 1 to heat a home with the geothermal heat pump or air source heat pump is more efficient way than with electric baseboard. It is clear the save made by heat pump into the home heating bills. In geothermal heat pump has COP 3.89. It means that heat pump and geothermal heat system takes one euro electricity to produce 3.89 euro heat into the house. At the same time, electric baseboard takes one euro electricity

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to produce one euro heat into the house if it has 100% efficiency. As seen Fig. 3 geothermal heat pump is good way for long-time to heating the houses because even though geothermal heat pump starting costs are expensive this system will pay back slowly. The energy is virtually free and environmentally friendly source comparing with other source of heat the home such as natural gas or wood or fuel oil. As seen Fig. 4 a simple stylized diagram of a heat pump's vapour-compression and refrigeration cycle. In the picture number one is condenser and number two is expansion valve. The three and four numbers are evaporator and compressor. This is the simple principle how the heat pump works. It can be use as cooling home in summer or heating home in winter with single unit.

$$COP_{heating(max)} = T_{hot} / T_{hot} - T_{cool}$$



Wood Stove	1 074 €
Pellet	722 €
Fuel Oil	820 €
Propane	1 556 €
Natural Gas	806 €
Electric Resistance	909 €
Air Source Heat Pump	501€
Geothermal Heat Pump	259 €

Figure 3. Estimated annual heating costs per heating system (J. Brown, 2016)

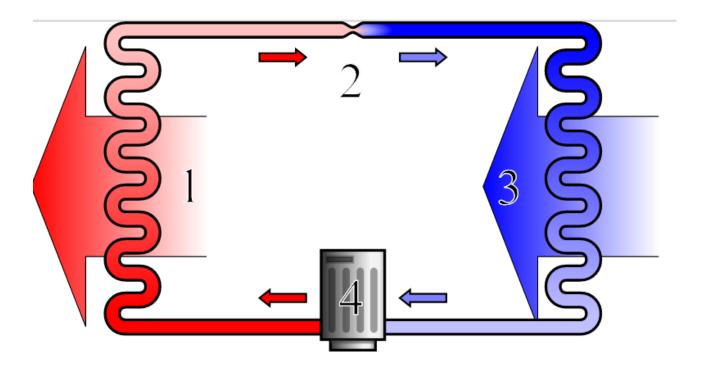


Figure 4. A simple stylized diagram of a heat pump (Wikipedia, 2016)

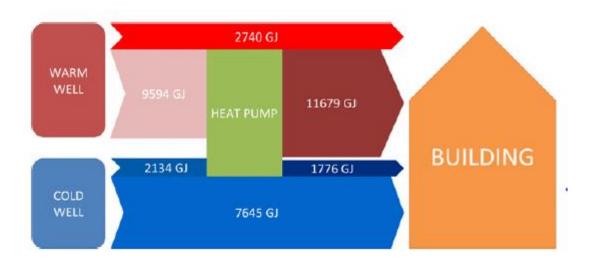


Figure 5. Energy flows with heat pump (D. Vanhoudt, J. Desmedt, J. Van Bael, N. Robeyn and H. Hoes, 2011)

In Fig. 5, a diagram from D. Vanhoudt and his term shows how COP for heating and cooling should be complied. The average COP_{heating} of 5.6 (11679/2085=5.6) is obtained for heat pump in the winter whereas in summer the number is 5. These values are excellent. The heat pump takes 9594 GJ energy from warm well and rest comes from electricity unlike electric baseboard heaters. It had given to the building 11679 GJ heat energy. That mean it had produced 2085 GT from electricity (11679-9594=2085). This way can able to calculate the heat pump's COP_{heating} of 5.6. Same way it takes 2134 GJ energy and it provides 1776 GT energy. Other hand heat pump had reduced 358 GJ (2134-1776=358) heat energy into cool. There for it has COP_{cooling} of 5.0 (1776/358=5). (D. Vanhoudt, J. Desmedt, J. Van Bael, N. Robeyn and H. Hoes, 2011). According to the Tee Itse magazine it has other benefits like it gives quality air in the house and it has lower maintenance cost to operate. Household heat pump is about 2000 euro and has 15-20 years of lifetime. The prices are comparable relative to other units.

2.3 The sensible thermal energy storage

Sensible heat storage (SHS) means that the materials do not change phase while heat storage or cool storage. This unchanged phase is including either solids or liquids. In order to store cool or hot fluids (liquid storage) need bulky tanks and expensive heat pumps. That could be an expensive process, that why usually solid media is used for a sensible storage. The valve of the storage density can be determine by storage media's specific heat and the temperature difference. Commonly water, brick, rock and soil are use as sensible energy storage materials (N. Yu, R.Z. Wang and L.W. Wang.)

According to N.Yu and his term's article sensible heat storage is the most common storage system used in recent years because of energy, demand has increased and developed in the excavation technology. That why it attracts urban or suburban builders. This concept commonly connects with solar driven systems. That mean it has environmentally friendly concept. It has four different methods for storing thermal energy. Those are borehole thermal energy storage (BTES), aquifer thermal energy storage (ATES), hot water thermal energy store (HWTES) and gravel-water thermal energy store (GWTES) as seen Fig. 6.

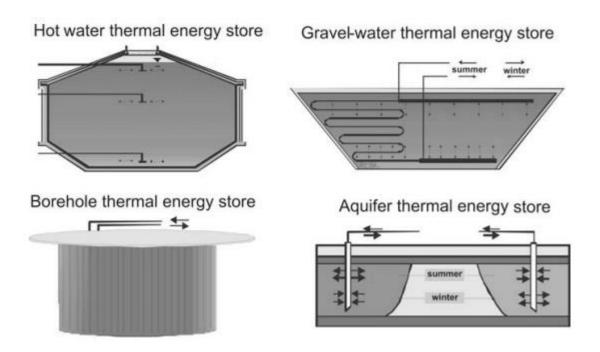


Figure 6. Types of seasonal thermal energy stores (D. Bauer et al, 2010)

2.3.1 Borehole thermal energy storage (BTES)

Borehole thermal energy storage is storing heat energy into the borehole. The ground is the storage media. The storage volume cannot be separated form ground. This is done by drilling vertical holes into the ground. Common storage materials are rock or water saturated soil. The depths of the boreholes are variable, that ranges from 30-100 m, and it has 3-4 m between the two holes. Nowadays these depths are gone even deeper. The deeper holes are better because of the flow of heat from the earth interior. In the Fig. 10 shows how the depth below surface and temperature increases clearly.

In the borehole there is pipe build in the borehole and the pipe carries heated liquid in or out from the hole. This pipe can built in three different ways. Those are double or single u-pipes and concentric pipe. The pipe is usually made of synthetic material. For instance, high-density polyethylene (HDPE) is one of those materials. In the Fig. 7 can see the different pipe systems feed to the borehole. Single u-pipes work as one single pipe go in to the bottom of borehole and U-turn and return same pipe. The double u-pipe is with two pipes go in and U-turn in the same hole. Other hand concentric pipe system work as small diameter pipe go in to hole and U-turn with big pipe, which is, surround by small diameter pipe.

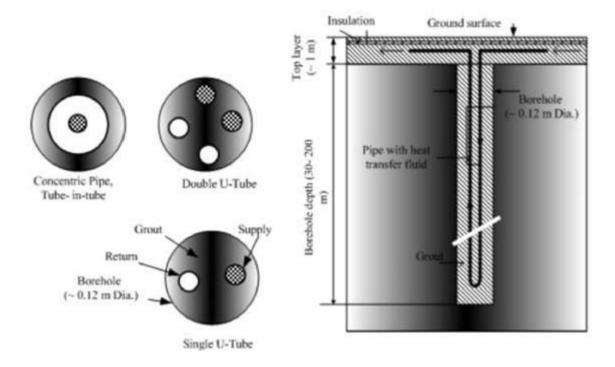


Figure 7. Different types of borehole heat exchangers (F. M. Rad and A. S. Fung, 2016)

This system has some of the advantages comparing with other systems. It has high thermal capacity, good operation characteristic, good thermal stratification, not toxic and non-flammable, lower heat losses, free large area to storing heat, repair possible and easy to maintenance. Also it has disadvantages. It is overall expensive system comparison with other sensible thermal energy source. In addition, it need more space than other source. It can able to give about 15-30 kWh for cubic meter space and for instance hot water thermal energy storage gives 60-80 Kwh as seen table 4. In the pipe the fluid, that is moving mostly water or water mix with ethanol or glycol. The holes are normally fill with bentonite or quartz with sand or water-saturated claystone mixture.

Quartz has advantage that it has higher thermal conductivity. Quartz has thermal conductive of 1.0–1.5 W/mK and water- saturated claystone mixture has 0.6 W/mK.

According to F. M. Rad and his team's article claystone or water-saturated claystone are best media for borehole thermal energy storage. It has high heat capacity. This system's efficiency depends on how much heat injected and extract from ground. Average it has about 40-60% efficiency. This mean it loses about 40-60% of injected heat into the ground. The efficiency also is depending on depth of hole and between two holes horizontal distances. B. Welsch's graph shows the maximum distances between two boreholes and earth rocks thermal conductivity are affecting the efficiency of all system.

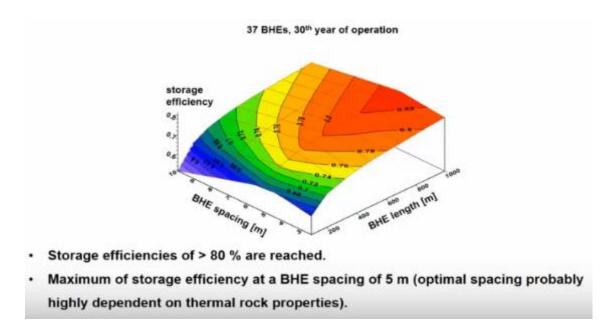


Figure 8. Borehole thermal energy storage efficiency (B. Welsch, 2015)

This system has good future because of it can be added with new holes to existing boreholes when energy needs grow and it is simple process comparing with other systems. According to the Henrik Holmberg and his team's article there are two ways increasing the heat capacity. Those are increasing boreholes or increasing borehole depths. For urban areas, better option is increasing borehole depths. For this, reasons in Norway and Sweden 400-500 m holes built on the commercial basis. In Scandinavia, the temperature increases 1-3 K/100 m. When the holes get deeper heat, extraction is

higher and the same time cooling loss decreases, which is good for Scandinavian countries. Also this system has low quality heat that why it has to be connected to heat pump to get the better quality heat. This concept is shown in the Fig. 9. In Rhein-Main area, Germany commercial building is using heat pump technology with deep boreholes (200 m deep) in recent years. (P. Jiang, X. Li, R. Xu and F. Zhang)

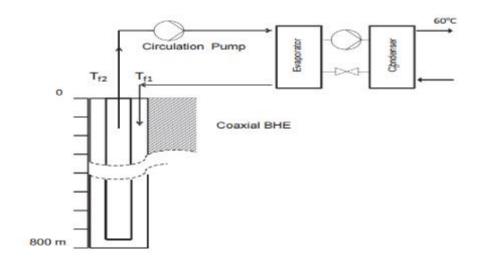


Figure 9. Heat pump performance in deep borehole heat exchangers (H. Holmberg, J. Acuna, E. Naess and O. K. Sonju, 2016)

The borehole heat output not only depends on the deep of the hole. There are number of other thing play a role too. Those are bore diameter, pipe diameter, flow rate of the fluid, temperature of the fluid, tape of fluid, number of holes and number of loops in the well. Top of these things also storage heat energy can be determined by what is the materials thermal conductivity, temperature difference between fluid and the storage media and thickness of the media where the heat is stored as shown in the formula below. The best way to get high efficiency is relay on the optimization between all those things in the above. This way can be minimizing borehole depth and cost.

The available heat flow is given by $q = K_t \Delta T/z$

Where

q is the heat flow per square meter in W/m^2

(2)

 K_t is the thermal conductivity of the rock in $W/m/^{\circ}C$

 ΔT is the temperature difference in degrees centigrade

z is the thickness of the hot rocks layer in meters

(P. Jiang, X. Li, R. Xu and F. Zhang)

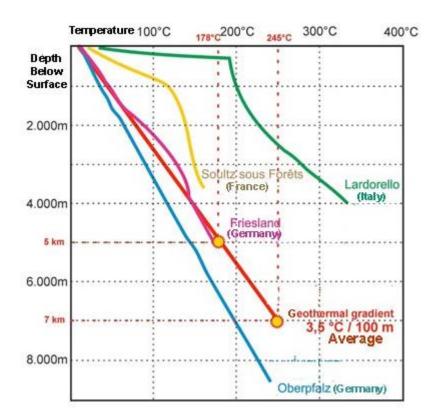


Figure 10. Earth crust temperature profile at difference location (Mpoweruk, 2016)

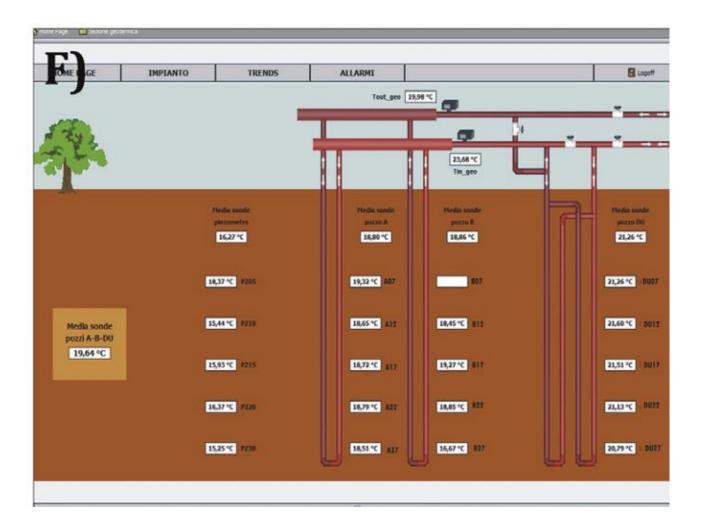


Figure 11. Two different plumbing and temperature with the depth (N. Giordano, C. Comina, G. Mandrone and A. Cagni)

According to the N. Giordano and his team's article, connecting tens or hundreds of boreholes to the heat pumps are done by two different ways. Those are double U tube or single U tube as shown in Fig. 11. These systems have different temperature with the depth but double U tube does not have the double efficiency than the single U tube. The reason is earth thermal conductivity.

2.3.2 Aquifer thermal energy storage (ATES)

Aquifers are porous media, which is water with sand, sandstone, igneous or metamorphic rock. Underground water (aquifers) must be low flow or no flow so that it could be a thermal storage. At least two or more wells have to drill in order to injecting

or extracting heat. As shown Fig. 12 and 13, the aquifer thermal energy storage system works same as borehole thermal storage system. The water from the aquifer pumped into the heat pump and then returns back to aquifer in some distance location.

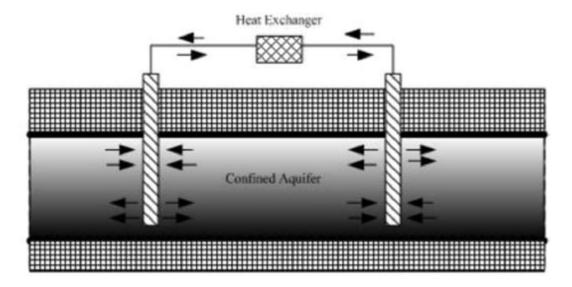


Figure 12. Aquifer thermal energy storage (F. M. Rad and A. S. Fung, 2016)

According to F. M. Rad and A. S. Fung, article aquifer thermal energy storage system is changes with the outside temperature (T_{ambient}). As shown Figs 14, 15 and 16 the system works as heater and cooler in one unit. The heat from aquifer pumped into the storage tank in the hospital for heating water and heating the building. In summer months, it works as cooling the hospital building. When the temperature more than 14°C outside then cool side of the pump (in the Fig. 14 shown as blue colour) started working. It goes thought the heat pump and brings cooler air to the building. In the below 4°C outside temperature it happens opposite way as shown Fig. 16 red color. In addition, it can stored the heat in the reserve tank whenever the temperature outside is between 4°C to 14°C. This diagram has been shown in the Fig. 15. This system is successfully working in Belgium capital Brussel's public hospital.

Unlike Brussel's public hospital system the Berlin Germany, parliament building has two separate these systems. One system has with 60 m depth and other one has with 300 m depth. The 60 m depth aquifer thermal energy storage is being use as bring cool air to building and other one for heat to the building in winter months. To bring heat to the building low surface to volume ratio is used and high surface to volume ratio for

cooling the building. In order to get the best efficiency from this system all the physical and chemical parameters of the aquifer have to know. The parameters changes with places and aquifer properties.

Also the aquifer has to have less heat loss in the surrounding. It means that surface to volume ratio have to be low as possible. The heat loss usually is due to either conduction or convection. In the fluid Rayleigh number which is giving a point where it changes to conduction or convection. It varies with fluid thickness. As aquifer, thickness is changing with place as Rayleigh number and efficiency are changing. This is shown clearly in the Fig. 17. The distance between inject pipe and production pipe are playing big role on the efficiency. Other important aspects are considering about efficiency the clay surrounding the aquifer well and how depth. Heat pump efficiency is important to recover most of the heat. Also type of pipe construction is important for efficiency. There are two type pipe constructions available. Those types are shown in the Fig. 13. The close loop pipe construction fluid inside the pipe dose not mix with outside aquifer but open loop pipe construction fluid inside the pipe is same as well fluid (aquifer). The panel A (Fig.13) is bringing heat from aquifer in winter with open loop and panel B is bringing cool from aquifer outside.

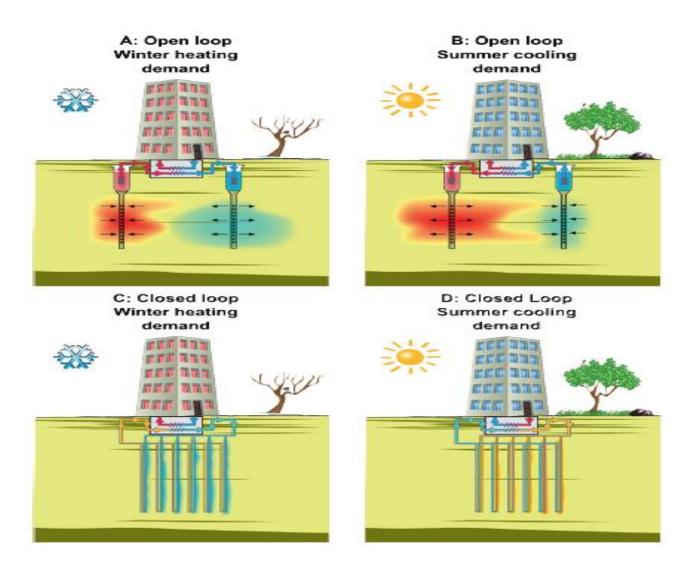


Figure 13. Different types of aquifer thermal energy storage systems

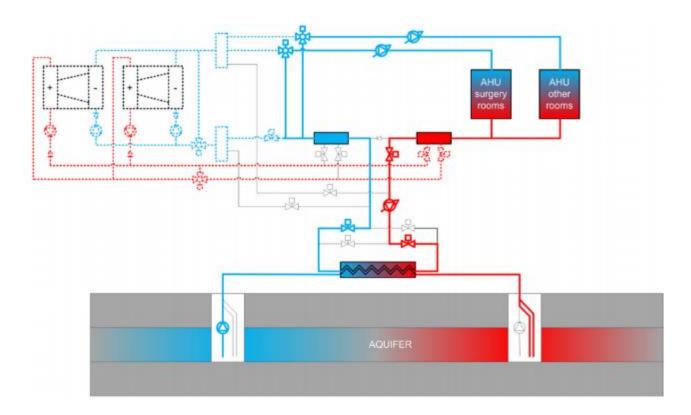


Figure 14. Hydraulic scheme of the installation in cooling mode $(T_{ambient} > 14 \circ C)$ (D. Vanhoudt, J. Desmedt, J. Van Bael, N. Robeyn and H. Hoes, 2011)

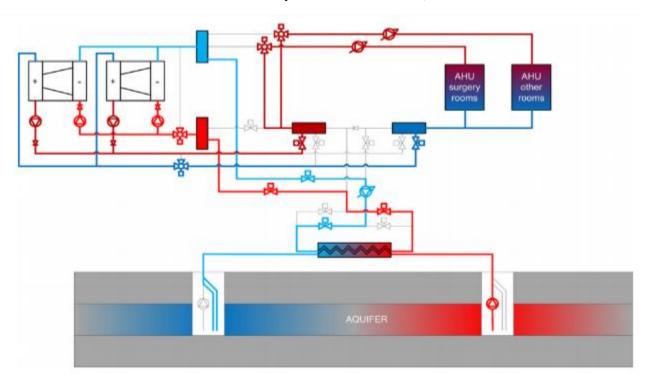


Figure 15. Hydraulic scheme of the installation in heating mode $(4 \circ C < T_{ambient} < 14 \circ C)$ (D. Vanhoudt, J. Desmedt, J. Van Bael, N. Robeyn and H. Hoes, 2011)

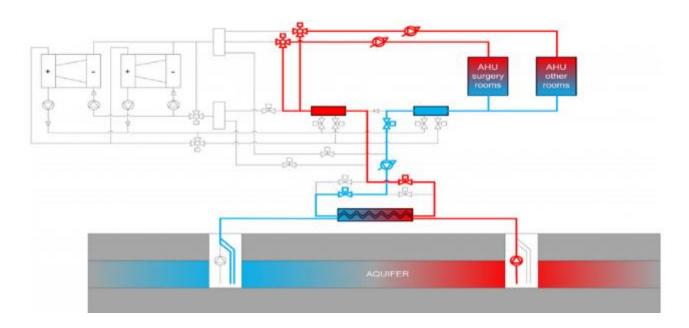


Figure 16. Hydraulic scheme of the installation in regeneration mode ($T_{ambient} < 4$ °C) (D. Vanhoudt, J. Desmedt, J. Van Bael, N. Robeyn and H. Hoes, 2011)

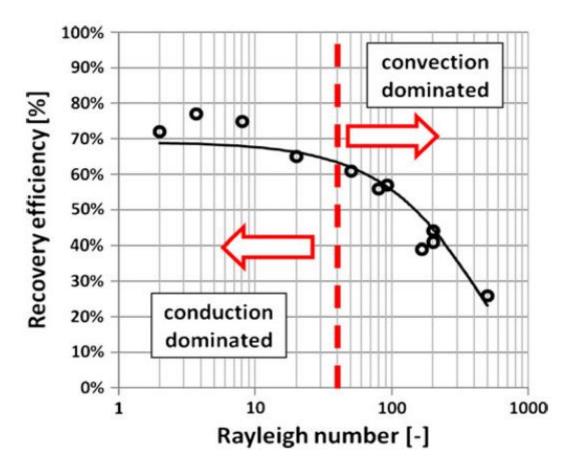


Figure 17. Recovery heat efficiency from aquifer thermal energy storage and Rayleigh number (G. Schout, B. Drijver, M. Gutierrez-Neri and R. Schotting)

2.3.3 Hot water thermal energy storage (HWTES)

The geological conditions almost play no role in hot water thermal energy storage. It has tank with water and the tank is usually constructed of reinforced concrete or steel or high-density concrete without inner steel-liner. Inside the tank is insulted granulated foam glass in textile bags. These materials give drying capability, easier and faster installation. The water has virtually free and has good values for specific heat capacity as shown Table 5. Top of that it has good power for charging and discharging (F.M. Rad, A. S. Fung).

The tank has two different temperatures. The cooler temperature water naturally goes to bottom and hotter temperature water to the top of the tank. However, the tank cannot get cooler than 0°C because of the water freezing point. There are two pipes in the cooler bottom and two pipes in the hotter top of the tank. There pipes than were connected to heat pump and solar collector as shown Fig. 18. These systems use solar collector and heat pump to achievements better efficiency.

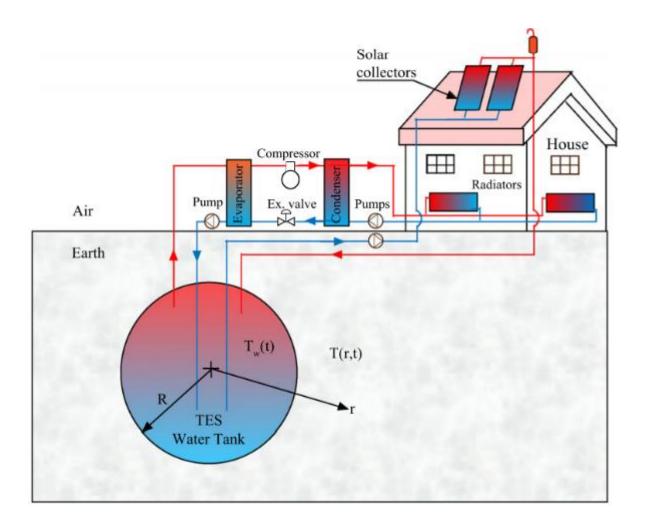


Figure 18. House heating system with heat pump and underground thermal energy storage (TES) tank (R. Yumrutas, M. Unsal, 2012)

In the newer version has optimized flexible pipes which move up and down to get the right water temperature of the water for right heat need. There are two kind of storage system available in HWTES. Those are single storage and multi storage as shown in the Fig. 19 and Fig. 18. Single storage system heats only one particular house with single storage. Water tank have two different temperatures as seen Fig. 18 that in bottom colder than top of tank. Tank has four different pipes. For instant in winter hot part of tank (the heat produce by solar heater) pumps to heat pump and get to house to heat the house. The return water from house cooler water goes back though heat pump and bottom of the tank. In summer, this system works opposite direction in order to cool the house.

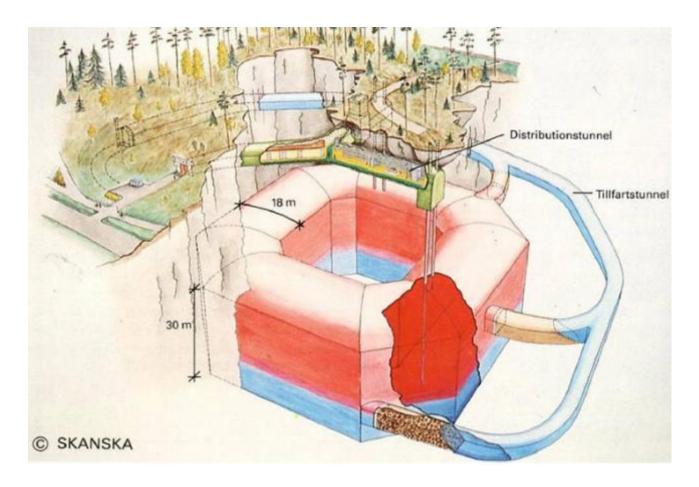


Figure 19. Layout of the Lyckebo rock cavern in Sweden (D. Park, H.M. Kim, D.W. Ryu, B.H. Choi, Ch. Sunwoo and K.C. Han, 2013)

The multi storage system as shown Fig. 19 has much larger tank than single storage system and has two or three parts to store different temperature water. This system serves the heat for whole village or town.

Table 2.Properties of the geological structures (R. Yumrutas and M. Unsal, 2012)

Earth type	Conductivity (W/m K)	Diffusivity (m ² /s)	Specific heat (J/kg K)	Heat capacity (kJ/m3 K)
Coarse graveled	0.519	1.39×10^{-7}	1842	3772
Limestone	1.3	5.75×10^{-7}	900	2250
Granite	3.0	14.00×10^{-7}	820	2164.8

BTES has higher storage volume than HWTES. Typically BTES size is 3-5 time larger. According to F.M. Rad and A.S. Fung BTES article with volume of $35,000~\text{m}^3$ has 144 boreholes (38~m depth) while equivalent HWTES would requires $8700~\text{m}^3$.

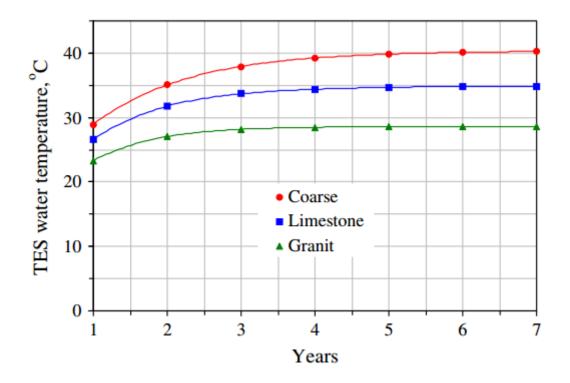


Figure 20. Annual temperature variation (R. Yumrutas and M. Unsal, 2012)

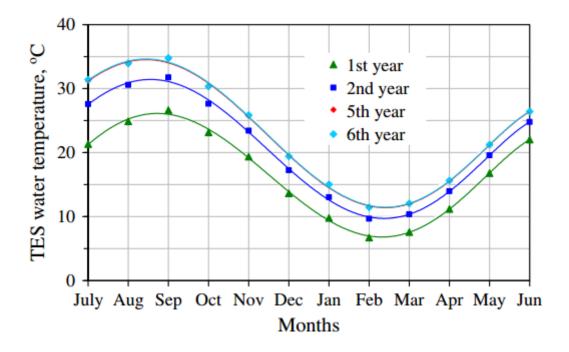


Figure 21. Annual temperature variation with number of operation years (R. Yumrutas and Unsal, 2012) M. 40 TES water temperature, °C Coarse 40 CE = 0.3TES water temperature, "C Limestone ■ CE = 0.4 30 ▲ Granite 30 ▲ CE = 0.5 20 20 10 10 July Aug Sep Oct Nov Dec Jan Feb Mar Apr May Jun July Aug Sep Oct Nov Dec Jan Feb Mar Apr May Jun Months Months

Figure 22. Effect of CE & earth type (R. Yumrutas and M. Unsal, 2012)

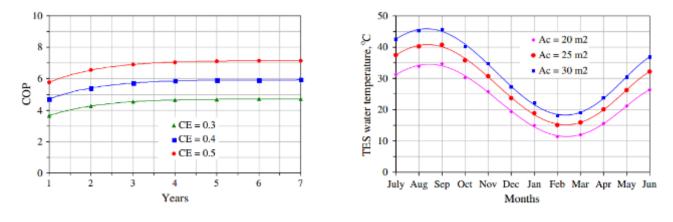


Figure 23. Effect of CE on COP (R. Yumrutas and M. Unsal, 2012)

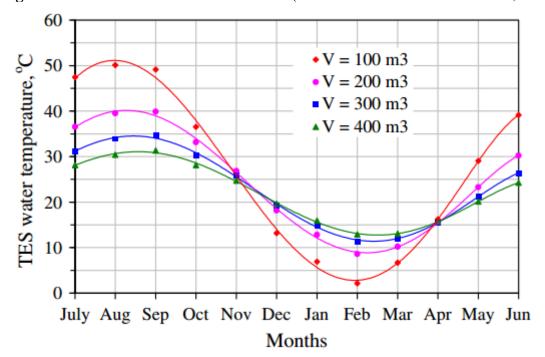


Figure 24. Effect of storage volume (R. Yumrutas and M. Unsal, 2012)

The Fig. 20 is displays with TES tank with different stones annual water temperature variation. At the same time Fig. 21 shows different age TES tank and there annual water temperature variation. Then as seen Fig. 22 effect of CE and ground type on annual temperature variation of water in the TES tank during fifth year of operation and Fig. 23 shows effect of CE on COP and collector area of the heat pump. All these research has been done in limestone and area of 20 m². Also all the test done in CE at 40% and Fig. 20-23 volume was 300 m³. However in the Fig. 24 clearly visualizes how storage

volume effect on annual water temperature for a period of 5 years (R. Yumrutas and M. Unsal, 2012).

HWTES and gravel-water thermal energy storage (GWTES) efficiency depend on tank's surrounding material, tank's size, tank's area and years of serves. Underground storage tank surrounding material coarse has better storage heat about 40°C for a seven year period. This mean coarse (one type of ground or soil) has slower heat loss rate than limestone or granite. Also mean coarse has lower conductivity value and higher heat capacity value than limestone or granite as seen Fig. 20. In winter underground water tank temperature has, able to keep up over 10°C with coarse has 13°C. This is positive result and with the heat pump helps able to heat the house in winter as seen Fig. 22. Also six years been in use tank have higher temperature water than one year in use tank as seen Fig. 21. Other hand surface area also makes different in the underground storage water tank temperature as seen Fig. 23. Volume of the tank make different too but if winter use better to have large volume tank because of 400 m³ volume tank have 10°C different with 100 m³ volume tank as seen Fig. 24. The materials are found in common underground surfers and have different properties. These properties play big role into storage heat. Coefficient of performance (COP) different between CE 0.5 and CE 0.3 are big about 2.5 COP gain as seen Fig. 25.

2.3.4 Gravel-water thermal energy storage (GWTES)

Gravel-water thermal energy storage is same as hot water thermal energy storage but this is cheaper system. It has gravel and sand or soil mixture mix with water. The pipes carries the water from tank to heat pump is made of plastic. The maximum operating temperature of the water is 95°C. The tank has 50% bigger in size than the hot water thermal energy storage tank (F. M. Rad, A. S. Fung). The advantages of this system are that low static requirement and simple store cover. The disadvantages of this system are that thermal capacity is low and different charging system. Also it has buffer storage and maintenance or repair not possible because of it has sealed tank.

Table 3. The thermal and physical properties of storage media for the HWTES and GWTES (N. Uddin, 2012)

	Water (at 20°C)	Gravel-water mixture
Porosity	-	0.37-0.43
Density [kg/m³]	992.2	1950-2050
Specific Heat Capacity [kJ/(kgK)]	4.18	2.0-2.2
Thermal Conductivity [W/(mK)]	0.63	1.8-2.5

As seen Table 3 HWTES have only water and water have twice higher specific heat capacity than GWTES. Which makes HWTES has more efficient way storage heat than GWTES. In addition, GWTES has porosity (spaces in a material). If thermal conductivity is small better energy storage material, there for HWTES has better way to storage energy than GWTES (Nasim Uddin, 2012).

Table 4.HWTES, GWTES, ATES & BTES comparison (F. M. Rad, A. S. Fung, 2016)

	HWTES	GWTES	BTES	ATES
Storage medium	Water	Gravel-water	Ground material	Ground material/water
Heat capacity (kW h/m3)	60-80	30-50	15-30	30-40
Storage volume for (1 m ³ of water equivalent)	1 m ³	1.3-2 m ³	3–5 m ²	2–3 m ³
Geological requirement	 Stable ground conditions 	 Stable ground conditions 	 Drillable ground Groundwater favorable 	 Natural aquifer layer with high hydra- ulic conductivity
	 Preferably no groundwater 	 Preferably no groundwater 	 High heat capacity High thermal conductivity 	 Confining layers on top and below No or low natural groundwater flow
	• 5-15 m deep	• 5–15 m deep	 Low hydraulic conductivity Natural ground-water flow 1 m/s 30–100 m deep 	Suitable water chemistry at high temperatures Aquifer thickness 20–50 m

As seen Table 4 comparison of different storage concepts Hot Water Thermal Energy Storage (HWTES), Gravel-water thermal energy storage (GWTES), Aquifer thermal energy storage (ATES) and Borehole thermal energy storage (BTES) (F. M. Rad, A. S. Fung, 2016).

In Table 4 it can see clearly borehole thermal energy storage (BTES) has less heat capacity that mean need more space to save the heat than other storage systems. Hot water thermal energy storage (HWTES) is best system to saving space and storage heat. Borehole thermal energy storage need more space to product energy than other three systems. Also aquifer thermal energy storage and Borehole thermal energy storage need deeper holes than hot water thermal energy Storage and gravel-water thermal energy storage as seen Table 4. If all the four sensible thermal energy storage system were

using water as transfer fluid then the power (Q) extracted from the wells were given following equation.

$$Q = cG(t_1-t_2)$$

Q = heating quantity under geothermal well (power) [kW]

c = specific heat of water [c = 4.187 kJ/kg °C]

 $G = flow \ rate \ [kg/s]$

$$t_1, t_2 = inlet water temperature, outlet water temperature [°C]$$
 (3)

(W. Wang and X. Zhang.)

Table 5. Comparison of the heat capacities with temperature differences of some possible storage materials.

Storage material	density $ ho$	mass m	specific heat C	stored energy Q					
	(kg/m³)	(kg)	(J/kg*K)	(J) (Δt=1 ^O C)	(J) (Δt=2 ^O C)	(J) (Δt=4 ^O C)	(J) (Δt=6 ^O C)	(J) (Δt=8 ^O C)	(J) (Δt=10 ^O C)
water	1000	1000	4182	4182000	8364000	16728000	25092000	33456000	41820000
clay	1281	1281	1381	1769061	3538122	7076244	10614366	14152488	17690610
gravel-water	2002	2002	2100	4204200	8408400	16816800	25225200	33633600	42042000
sand	1442	1442	830	1196860	2393720	4787440	7181160	9574880	11968600
coarse gravel	1505	1505	1842	2772210	5544420	11088840	16633260	22177680	27722100
limestone	1457	1457	900	1311300	2622600	5245200	7867800	10490400	13113000
granite	2691	2691	820	2206620	4413240	8826480	13239720	17652960	22066200
asphalt	1041	1041	920	957720	1915440	3830880	5746320	7661760	9577200
cement	2100	2100	880	1848000	3696000	7392000	11088000	14784000	18480000
soil	1840	1840	1140	2097600	4195200	8390400	12585600	16780800	20976000

$$Q = cm\Delta t = c\rho V\Delta t \qquad (\rho = m/V)$$

c = specific heat [c]

m = mass of the storage material [kg]

 Δt = temperature different between before and after storing energy [^{O}C]

V = volume of the storage material [m³]

$$\rho = density of the storage material [kg/m3]$$
 (4)

Even though, water has the good energy storing capacity. There are other storages materials commonly available. Those are shown in the table 5. In the table all the materials volume had been calculated as one cubic meter. Heat capacity (Q) is the

energy that the material storages during the temperature raise. In addition, heat capacity had been shown with six different the temperature rise. Nevertheless, all the energy, which has stored cannot be recover but at least 20% can be recover. This is good amount of energy compare with the space uses. The temperature rise (different) can be happen for instanced by heat up with directly by sun light or with solar collector. As mentioned above there are other systems available to storage energy. One of these systems is mechanical energy storage system.

2.4 Mechanical energy storage system

Mechanical energy storage system needs large excavation. Some time it can be 1500 m in depth. Usually the utility companies use this system to support the daily and weekly fluctuation in power demand. For example, water pumped into tank with high elevation when demand is low. When demand is high, it flows into lower elevation (underground tank) at the same time it turns generator. The off-peak electricity could be hydroelectric or solar panel or wind turbine. All these energies are renewable and seasonal. According to the N. Uddin article, strip-mined areas are in use as artificial lake and it has been in use as underground pumped hydro (UPH) concept.

The compressed air energy storage (CAES) are same way as underground pumped hydro but it has compressed air pumped into cavern instead of water. The compression happens during off-peak demand periods. There are two kind of air storage available now. Those are compensated-nearly constant air pressure and uncompensated-constant air volume with varying pressure. The problem with this system is that rock mass permeability is causing the caverns leak and it is costly to fix.

Underground gas storage system (UGS) is same than other two. This system can be used as pressurized gas for gas supply and same time it could be energy storing component. It is one system with two different reasons. Other advantages are lower pollution, lower maintenance and better load balancing. In addition, this is safe way of

energy delivery and has more shallow depth caverns than other mechanical energy storage systems (N. Uddin, 2012).

2.5 Latent heat storage: Phase change material (PCM)

According to the N. Yu and his term's article, the latent thermal storage is storing energy by phase change process of a material at a constant temperature. As mentioned earlier most popular storage systems are sensible and latent heat storage. Latent heat storage is more appealing to the senses than sensible heat storage because of it has high storage density as shown Fig. 31 and smaller temperature different. This system is delivering the energy to the storage material effectively unlike in sensible heat storage, where the energy is stored by elevating the temperature of the storage material. In order to understand latent heat storage first has to understand the phase change.

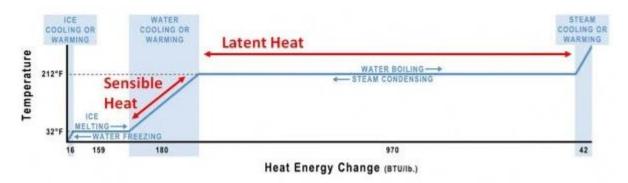


Figure 25. Water temperature changes with added heat (C. Hall, 2017)

It is internal energy relating to the phase (solid / liquid / gas) of a material and does not affect the temperature as shown Fig. 24 and 25. This system needs a storage material that has high specific heat capacity and latent heat values in order to work well. Following equation imported to calculating the energy of the phase changing materials.

 $Q_1+Q_2+Q_3+Q_4=0$ (only insulated or no heat energy losses)

 $Q_1 = mc\Delta T = medium \ warming \ or \ cooling \ energy$

 $Q_2 = mL_f = medium \ latent fusion or melting energy$

 $Q_3 = mL_v = medium\ latent\ vaporization\ energy$

 Q_4 = heating source (example solar heater or solar collector or electrical stove) energy

c = specific heat

m = medium mass

 ΔT = medium temperature different

 $L_f = latent heats of fusion$

$$L_{v} = latent \ heats \ of \ vaporization$$
 (5)

As seen Fig. 25 and Fig. 26 for instance if the media is water than Q_2 would be ice melting, Q_1 would be water which is heated to 0° C to 100° C, Q_3 would be water boiling to be vapor and Q_4 would be electrical stove energy. Heat capacity means how much heats can the material (1 kg) able to transfer from hot to cool media. Heat capacity or thermal capacity is a measurable physical quantity. It is equal to the ratio of the heat. When heat added or removed from an object. Heat will change the temperature of the object that is call materials heat capacity. Often heat capacity simply called specific heat per unit mass of a material.

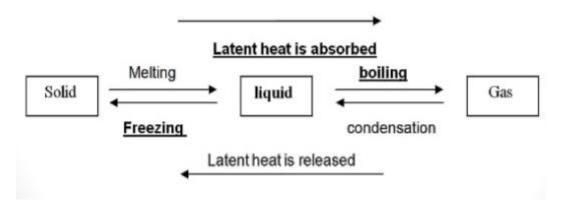


Figure 26. Latent heat absorbent and release (SlideShare, 2017)

Table 6. Material specific heat capacity and volumetric heat capacity (Maricopa, 2017)

Substance	S.H.C	S.H.C	Density	Volumetri H.C
	J/kg.K	cal/kg.K	kg/m³	kJ/m ³ .K
Water (0°C to 100°C)	4186	1000	1000	4186
Methyl Alcohol	2549	609	792	2018.8
Ice (-10°C to 0°C)	2093	500	917	1919.3
Steam (100°C at 1Bar)	2009	480	0.59	1.2
Benzene	1750	418	660	1155
Wood (typical)	1674	400	750	1255.5
Soil (typical)	1046	250	1840	1924.6
Air (50°C)	1046	250	1109	1160
Aluminum	900	215	2723	2450.7
Marble	858	205	2711	2326
Glass (typical)	837	200	2500	2092.5
Iron/Steel	452	108	8225	3717.7
Copper	387	92.4	8900	3444.3
Silver	236	56.4	10490	2475.6
Mercury	138	33	13593	1875.8
Gold	130	31	19320	2511.6
Lead	128	30.5	11341	1451.6

There are three different heats imported every material. Those are specific heat latent heats of fusion and vaporization. Especially in latent heat storage calculations these are imported values as seen Table 6. For instance, 1 kg ice is in -10°C to melt 0°C need 20930 J of energy (2093*10 =20930 J from Table 6). The same 1 kg water is in 0°C to 100°C need 418600 J energy (4186*100 =418600 J from Table 5) energy. That water is than boiled to steam and the steam final temperature is 150°C. It needs 100450 J of energy (2009*50 = 100450 J from Table 6) to do this processes. Over all 1 kg -10°C ice is heated to steam need 540 kJ energy (20930 J + 418600 J + 100450 J =539980 J = 540 kJ). In ideal world, which is no heat loss world for example, if solar collector heat up 1kg water to steam and use it in later time other word latent storage. There is 540 kJ of energy available to use in the ideal condition for a later time.

Table 7. Latent heats of fusion and vaporization (Utexas, 2016)

Substance	Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)	
Helium	- 269.65	5.23×10^{3}	- 268.93	2.09×10^{4}	
Nitrogen	-209.97	2.55×10^{4}	-195.81	2.01×10^{5}	
Oxygen	-218.79	1.38×10^{4}	-182.97	2.13×10^{5}	
Ethyl alcohol	-114	1.04×10^{5}	78	8.54×10^{5}	
Water	0.00	3.33×10^{5}	100.00	2.26×10^{6}	
Sulfur	119	3.81×10^{4}	444.60	3.26×10^{5}	
Lead	327.3	2.45×10^{4}	1 750	8.70×10^{5}	
Aluminum	660	3.97×10^{5}	2 450	1.14×10^{7}	
Silver	960.80	8.82×10^{4}	2 193	2.33×10^{6}	
Gold	1 063.00	6.44×10^{4}	2 660	1.58×10^{6}	
Copper	1 083	1.34×10^{5}	1 187	5.06×10^{6}	

Table 8. A list of selected solid – liquid materials for sensible heat storage (E. Milisic, 2013)

Material	Fluid type	Temperature range °C	Density (kg/m³)	Specific heat (J/kg K)
Rock	Solid	20	2560	879
Brick	Solid	20	1600	840
Concrete	solid	20	1900-2300	880
Water	Liquid	0-100	1000	4190
Caloriea HT43	Liquid (Oil)	12-260	867	2200
Engine oil	liquid	Up to 160	888	1880
Ethanol	Organic liquid	Up to 78	790	2400
Proponal	Organic liquid	Up to 97	800	2500
Butanol	Organic liquid	Up to 118	809	2400
Isotunaol	Organic liquid	Up to 100	808	3000
Isopentanol	Organic liquid	Up to 148	831	2200
Octane	Organic liquid	Up to 126	704	2400

Water has high specific heat. The specific heat is the heat that was stored inside the transfer fluid. This mean water is one of best heat transfer fluid and heat storage material as seen Table 8. Every latent heat thermal energy storage system requires a suitable phase changing material for use in a particular kind of thermal energy storage application. One of the important factors is to be consider when choosing an appropriate phase changing material is the life of the phase changing material, for example, its ability to resist change in the melting temperature and latent heat of fusion with time due to thermal cycling. In the Table 9 is showing different kind of salt hydrates to be

use as latent heat storage materials and properties. The properties T_m , H_m , ρ and C_p are follows temperature solid to liquid, latent heat, density and special heat.

Also there are the things makes different when it comes to choice the material for latent heat storage and their prices are import roll in order to choice the right salt as shown in Table 10. Salt hydrates have some advantages and disadvantages than other phase changing material. The advantages of salt hydrates are high latent heat of fusion per unit mass and volume (higher than paraffin), high thermal conductivity (compared with paraffin), have sharp phase change temperature, small volume changes during melting, high availability and low cost. One of the disadvantages is its hydrates or dehydrates affects which is reducing the volume that is available for thermal energy storage. Also in the freezing temperature it is forming crystals. This can be avoided by adding nucleating agent. Salt hydrates causes corrosion in metal containers, whereas metal containers are the common containers used in thermal energy storage systems.

Some of the phases, changing materials (other than salt hydrates) are generally ice, paraffin, fatty acids, salts and other mixtures. It has good storage density and much smaller temperature interval. The drawbacks are long-term stability of storage material, low thermal conductivity, phase segregation and sub cooling during the phase change process. All these phase changing material are ether organic or inorganic. For instance, the paraffin (D-Mannitol) is an inorganic phase changing material and a sugar alcohol (Erythritol) is organic phase changing materials. The Erythritol is one of the good phase changing material because of it has shown gradual degradation after 500 thermal cycles. There are number of different sugar alcohols available commercially. It has 90-190°C melting evaporating temperature and it is organic. D-Mannitol has a slightly lower value of latent heat of fusion than Erythritol; however, it has a higher melting point than Erythritol. Erythritol is common use as phase changing materials and as heat transfer fluid to the storage medium due to its high latent heat of fusion, its non-toxic nature and its easy availability (G.Kumaresan, R. Velraj and S.Iniyan).

Table 9. The most cited values of thermal properties of some salt hydrates to be used as latent heat storage materials (M. Kenisarin and K. Mahkamov, 2015)

	Tm (°C)	Hm (kJ/Kg)	$p (Kg/m^3)$	$p (Kg/m^3)$	Cp (kJ/Kg°C)	Cp (kJ/Kg°C)	k (W/m°C)	k (W/m°C)
			solid	liquid	solid	liquid	solid	liquid
Lithium chlorate tritydrate	8.1	253	1720	1530				
Potassium fluoride dihydrate	18.5	231	1447	1455	1.84	2.39		
Manganese nitrate hexahydrate	26	140						
Calcium chloride hexahydrate	29.5	170	1680		1.42	2.3		
	29.6	191	1802	1562	1.42	2.1	1.088	0.54
Lithium nitrate trihydrate	30	125						
	29.9	296						
Sodium sulphate decahydrate	32.4	251						
Sodium carbonate decahydrate	34	251	1440		1.88	3.35		
	33	247	1460					
Calcium bromide hexahydrate	34.3	116	2194	1956				
Zinc nitrate hexahydrate	36.4	130	2070		1.34	2.26		
Disodium hydrophosphate	36.5	264	1520		1.55	3.18		
dodecahydrate	35.2-44.6	280	1520	1442	1.7	1.95	0.514	0.476
Calcium nitrate tetrahydrate	42.6	140	1820		1.46			
	42.7	142						
Sodium thiosulfate pentahydrate	49		1690	1660	1.46	2.38		
	48.5-55.2	201	1750	1670				
	48	200						
Sodium acetate tritydrate	58	180	1450		1.97	3.35		
	58	289						
Cadmium nitrate tetrahydrate	59.5	106	2450		1.09			
Sodium hydroxide monohydrate	64	272						
Barium hydroxide octahydrate	78	301	2180		1.17			
	78	266						
	78	295						
Magnesium nitrate	90	160	1460		2.26	3.68		
hexahydrate	89.9	163	1636	1550	1.81	2.48	0.669	0.49
	116.7	169	1570	1450	2.25	2.61	0.704	0.57
Ammonium alum	94	269	1650		1.71	3.05		
Magnesium chloride	117	172	1560		1.59	2.85		

Table 10. Wholesale prices of salt and salt hydrates (produced in China and India) (M. Kenisarin, K. Mahkamov, 2015)

Salt	Purity (%)	Mimimal order (Metric ton)	Company (country)	FOB price USD/to
Pure salts				
Potassium fluoride	98	1	Shanghai Sungo Technology & Trade Co., Ltd. (China)	2800-3000
	99.3	25	Wuhan Xingzhengshun Import & Export Co., Ltd. (China)	1500-1600
	99	5	Tianjin Tiger International Trade Co., Ltd.	1500-1600
Calcium chloride	95	20	Weifang Dahe Snow-Melting Products Co., Ltd.	225-230
	94	5	Foodchem International Corporation	250-500
Lithium nitrate	99	i	Jiangxi Royal Import & Export Co., Ltd.	8350-9850
	99	0.001	Wuhan Rison Trading Co., Ltd.	7000-10000
	99	0.001	Haihang Industry (Jinan) Co., Ltd.	1000-3000
Sodium sulphate	99	25	Tianjin Credit International Co., Ltd.	98-110
Journal Sulphane	99	26	J&c Industry Corporation, Ltd.(nanjing)	87-90
	99.7	200	Sichuan Union Xinli Chemicals Co., Ltd.	70-200
Sodium carbonate	99.7	21	Zhengzhou Mahaco Trading Co., Ltd.	160-250
Sodium carbonate		20		
	99.2		Weifang Ruidesheng Chemical Co., Ltd.	203-208
	99.2	10	Wuhan Golden Fortune Technology & Trade Co., Ltd.	100-250
Disodium hydrogenphospate	97-99	10	Sichuan Mianzhu Ronghong Chemical Co., Ltd.	390-600
Calcium nitrate	99	10	DEE PEE CHEM INDUSTRIES	350-380
Sodium thiosulphate	99	25	Henan Eastar Chemicals Co., Ltd.	220-300
	98	20	Tianjin Xibeier International Co., Ltd.	160-200
	99	22	Ningbo V&S International Trade Shipping Co., Ltd.	220-280
Sodium acetate	99	25	Weifang Ocean Trading Co., Ltd.	950-1300
	99	25	Zouping Changshan Town Zefeng Fertilizer Factory	700-1100
	99	1	ULTRA CHEMICAL WORKS (India)	1000
Sodium hydroxide	99	27	Tianjin Shengxinhai Chemical Co., Ltd.	300-400
-	99	2	Tianjin Yuanlong Chemical Industry Co., Ltd.	350-437
	99	10	Wuhan Well Sailing Industry And Trade Co., Ltd.	400-600
Barium hydroxide	99	5	Richin International Trade (Dalian) Co., Ltd.	1000-2000
	99	10	Qingdao Yingfengyuan Industrial & Trading Co., Ltd.	755-936
	99	10	Tianjin Topglobal Technology Co., Ltd.	700800
Magnesium nitrate	99	50	Sichuan Yimin Fertilizer Co., Ltd.	245-300
and the same transfer	98	20	Xiamen Vastland Chemical Co., Ltd.	200-300
	98	1	Shanxi Wencheng Chemicals Co., Ltd.	290-340
Ammonium alum	99.3	25	Gansu Jinshi Chemical Co., Ltd.	100-200
Administration and the	99.7	25	Zibo Zichuan Chengpeng Chemical Factory	160-193
	99.3	20		
Calcium chloride			Humate (Tianjin) International Limited	150-300
Calcium chloride	98	20	Shouguang Jinlei Chemical Co., Ltd.	350-390
	99	5	Dalian All World I/E Co., Ltd.	250-630
	99.8	20	Liaoning Metals & Minerals Enterprise Co., Ltd.	150-300
Salt hydrates				
Calcium chloride hexahydrate	94-97	15	Zhengzhou Macro Imp. & Exp. Co., Ltd.	220-340
Sodium sulphate decahydrate	99.5	25	Zhengzhou Clean Chemical Co., Ltd.	70-120
Sodium carbonate decahydrate	99	20	Wuhan Guotai Hongfa Commodity Co., Ltd.	200-230
Calcium nitrate tetrahydrate	99	25	Shanxi Jiaocheng Tianlong Chemical Industry Co., Ltd.	255
Sodium thiosulphate pentahydrate	99	25	Dahua Group Dalian Guanlin International Trade Co.,	160-180
	99	5	Changsha Weichuang Chemical Co., Ltd.	285
Sodium acetate trihydrate	99.8	5	Foodchem International Corporation	500-600
•	99	1	Tianjin Flourish Chemical Co., Ltd.	400-892
Barium hydroxide octahydrate	99	10	Richin International Trade (Dalian) Co., Ltd.	700-800
Magnesium nitrate hexahydrate	98	25	Tianjin Crown Champion Industrial Co., Ltd.	230-250
o	98-99	1	Shanxi Wencheng Chemicals Co., Ltd.	240-280
Ammonium alum dodecobudente	99.5	25	Henan Allrich Chemical Co., Ltd.	300-500
Ammonium alum dodecahydrate				
Colobor obligate boundaries	99.5	12	Chance Sun Import & Export (Dalian) Co., Ltd.	177-300
Calcium chloride hexahydrate	98	20	Weifang Bell Chemical Co., Ltd.	90-120
	99	10	Weifang Menjie Chemicals Co., Ltd.	110-300

Other important latent heat thermal energy storage materials are salt and salt hydrate. Some of the salt and salt hydrates materials are Lithium chlorate trihydrate (LCT – LiClO₃ 3H₂O), Potassium fluoride tetrahydrate (PFT – KF 4H₂O), Manganese nitrate hexahydrate (MnNH – Mn(NO₃)₂ 6H₂O), Calcium chloride hexahydrate (CCH – CaCl₂ 6H₂O), Lithium nitrate trihydrate (LNT– LiNO₃ 3H₂O), Sodium sulphate decahydrate (Na₂SO4 10H₂O Glauber's salt – SSD), Sodium carbonate decahydrate (SCD – Na₂CO₃ 10H₂O), Zinc nitrate hexahydrate (ZNH – Zn(NO₃)₂ 6H₂O), Disodium

hydrogenphosphate dodecahydrate (DHPD - Na₂HPO₄ 12H₂O), Calcium nitrate tetrahydrate (CNT - Ca(NO₃)₂ 4H₂O), Sodium thiosulfate pentahydrate (STP hyposulphite – Na₂S₂O₃ 5H₂O), Sodium acetate trihydrate (SAT – CH₃COONa 3H₂O), Cadmium nitrate tetrahydrate (CNT – Cd(NO₃)₂ 4H₂O), Sodium hydroxide 3.5-hydrate and monohydrate (SHH_3.5 – NaOH 3.5H2O; SHM – NaOH H₂O), Barium hydroxide octahydrate (BHO - Ba(OH)₂ 8H₂O), Magnesium nitrate hexahydrate (MNH -Mg(NO₃)₂.6H₂O), Ammonium alum dodecahydrate (AAD – NH₄Al(SO₄)₂·12H₂O) and Magnesium chloride hexahydrate (MCH – MgCl₂.6H₂O – bishofite). These are good phase change latent heat materials (M. Kenisarin and K. Mahkamov). However inorganic salts with low melting points such as Na₂SO₄10H₂O, Na₂HPO₄12H₂O, Na₂CO₃10H₂O, CaCl₂6H₂O, and Na₂HPO₄12H₂O can be expected as best phase change materials because of their large amount of latent heat. Na₂SO₄10H₂O has especially large amount of latent heat (251 J/g) and is enough safety material to be use as food additive. Also there are other forms of phase change materials for instance alkanes which change their phases through liquid state (e.g. docosane, paraffin, etc.) and such as the solar salt (KNO3 40%–NaNO3 60%) and the high tech salt (KNO3 53%–NaNO3 7%–NaNO2 40%), LiNO3–KCl, etc. (C. Takai-Yamashita, I. Shinkai, M. Fuji and M.S. EL Salmawy).

These latent heat storage salts can be divide into three groups according to the temperature use. Those are low temperature heat storage (<120°C), medium temperature heat storage (120–300°C) and high temperature heat storage (>430°C). Most of phase changing materials which uses in solar thermal energy system are ether the low temperature or high temperature heat storage. Other hand in the industrial waste heat storage uses phase changing materials with a melting temperature between 120°C and 300°C. For instance in the food processing, paper production and textiles industry are good candidate for medium temperature heat storage system (D. Zhou and P. Eames).

Most recently discovered material like macroporous poly (ethylene dimethacrylate) (PEDMA) has cetyl alcohol, paraffin and silica. It has 75.6% paraffin and 23.1% cetyl alcohol and rest is silica. This makes the material high latent heat storage capacities and stopping the total leakage. Macroporous poly can able to storage about 133 J/g energy in this process. At the same time paraffin has about 90 J/g energy. Also macroporous

poly has able to with stand over 1000 heating and cooling cycle without leakages (T. Feczko, L. Trif and D. Horak). Even though macroporous poly is good latent heat storage material paraffin is one of the widely used materials. It is commonly available with reasonable cost. Also it has moderate latent heat storage density with a wide range of melting temperatures. This is shown as in the Table 11 (M. K. Rathodl and J. Banerjee).

All the phase changing materials that were mention in the top has specific heat capacity. For the phase changing material solid phase has smaller specific heat capacity than the liquid phase. This causes possibility to stores more sensible energy only if the material has low melting point. The two chosen salt hydrates are $CaCl_2 \cdot 6H_2O$ and $Na_2S_2O_3 \cdot 5H_2O$. Those have at least in theory bigger storage capacity than organic paraffin at $T_m = 60^{\circ}C$ and $C_{18}H_{38}$. Salt hydrates have better latent heat of fusion and specific heat capacity per volume than organic phase changing materials. These graphs are shown Fig. 27 (E. Milisic, 2013).

Table 11. Thermo-physical properties of the Phase change material (V. Pandiyarajan, M.Chinnappandian, V.Raghavan and R.Velraj, 2011).

Value
214 kJ/kg 1.85 kJ/kg K 2.384 kJ/kg K 0.4 W/m K 0.15 W/m K 856 kg/m ³ 775 kg/m ³ 58-60 °C

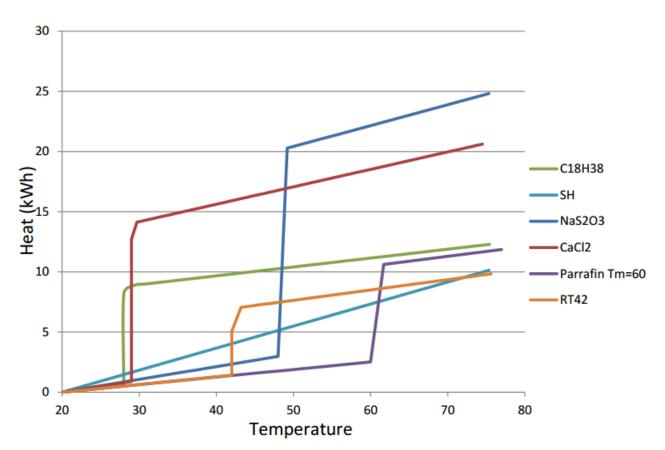


Figure 27. Comparison of different phase-change materials & the amount of stored energy (E. Milisic, 2013)

Table 12. Summary of molten salts below 300 °C (C.Y.Zhao, Y.Ji and Z.Xu, 2015)

Materials (mol%)	Melting point (°C)	Heat of fusion (kJ/kg)
LiNO ₃	253	373
(28.5–28.9)LiCl-(43.5–44.5)CsCl-(13.7–14.1)KCl- (13.3–13.5)RbCl	256 ± 2.5	375–380
59.15LiCl-40.85Ca(NO ₃) ₂	270	167
63LiOH-38LiCl	264	437
65.5LiOH-34.5LiCl	274	339
^a 33LiNO ₃ -67KNO ₃	133	170
^a 29LiNO ₃ -17NaNO ₃ -49.4KNO ₃ -4.6Sr(NO ₃) ₂	105	110
^a 58.1 LiNO ₃ –41.9 KCl	166	272
^a 57LiNO ₃ –43NaNO ₃	193	248
50NaOH-50KOH	169-171	202-213
30LiOH-70NaOH	210-216	278-329
20NaOH-80NaNO ₂	230-232	206-252
73NaOH-27NaNO ₂	237-238	249-295
87.3NaOH-6.1NaCl-6.6Na ₂ CO ₃	291	283
^a 87LiNO ₃ -13NaCl	208	369
86.3NaNO ₃ -8.4NaCl-5.3Na ₂ SO ₄	287	177
^a 53KNO ₃ -40NaNO ₂ -7NaNO ₃	142	80

a Weight percent.

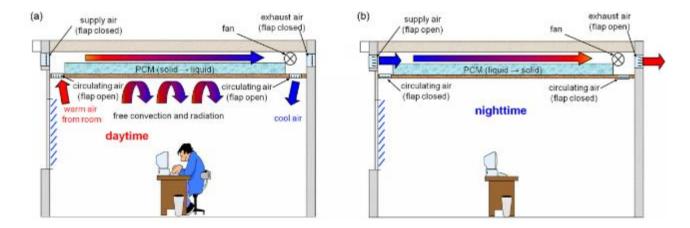


Figure 28. Cooling (a) and regeneration mode (b) of the ventilated cooling ceiling with Phase change material (H. Weinlädera, W. Körnera and B. Strieder, 2014)



Figure 29. Installation of the phase changing material boards in the conference room ceiling (H. Weinlädera, W. Körnera and B. Strieder, 2014)



Figure 30. phase changing material in ceiling board with salt inside (H. Weinlädera, W. Körnera and B. Strieder, 2014)

Thermal energy storage systems use widely phase change material because it can oborb and release lot of latent heat during phase change. There for this material can be put in 51

the walls, ceiling and floor of a building to minimize room temperature variations. This could lead to better living comport and at the same time energy saving (H. Weinlädera, W. Körnera and B. Strieder, 2014).

As earlier mentioned one of best way to get, the benefit from latent thermal storage system is use as building materials. For instance, it could ventilate (heating or cooling) ceiling with integrated phase change material as latent heat storage. In hot summer day time hot air from outside is blocked on purposely. This gives suspended ceiling phase changing material to change from solid to liquid. In nighttime outside cool air enter to the suspended ceiling ventilation and this gives the phase changing material to change from liquid to solid. This was research by H. Weinlädera and his team in Germany and the conference room was cool by 2K than the same kind of conference room without phase changing material in the suspended ceiling. This system's working diagram is shown in the Fig. 28. This system works in the wintertime too but the supply air is entering other way around and daytime there is sun shining. Therefore, the sun heat storage into roof panel as solid to liquid phase changes material. In the nighttime which time there are no sun and liquid change into solid as releasing energy to room and heat the room. In future, there will be invented even better materials and in this system has better future.

2.6 Thermochemical storage: Chemical reactions and sorption

2.6.1 Sorption

Thermochemical storage can be divide into chemical reaction and sorption. In this storage is able to storing big amounts of heat and it can able to be turn the other way round same process as shown in Fig. 32. This thesis is only analyzing sorption process. In a sorption process, heat is stored by breaking the securing force between the sorbent and the sorbate in terms of chemical potential. This process is beginning when the sorbent contacts sorbate. This is different from other methods of storing techniques. That why, this process did not require bulk vessels and it is good for long-term heat storage. It is good candidate for summer solar heat to winter use. There are four different sorption thermal storage systems those are liquid absorption, solid adsorption, chemical reaction and composite materials as seen Fig. 33. Liquid absorption material has two-phase and three-phase absorption. That means these three-phase absorption go thought melting and vaporization. Different between latent storage system and sorption storage system is sorption take half the less space than latent as seen Fig. 31. This is almost same like latent storage but with less space, more heat storage. This sorption is more compacted system then latent system although sorption is more expensive than latent system and sensible heat storage.

For instance according to N. Yu and his team's article this sorbent and sorbate process is almost same as chemical reaction which, give large amount of energy storage capacity. At the same time conventional material such as water need more three time the space than sorption heat storage system. This has been shown in the fig. 31. Even though, the water has high specific heat capacity. In addition, these systems can stores high temperature range. These positive things are given place on show in future with some extent of flexibility. For growing population and urban communities the space is hard to come by so this process would be good possibility in the future.

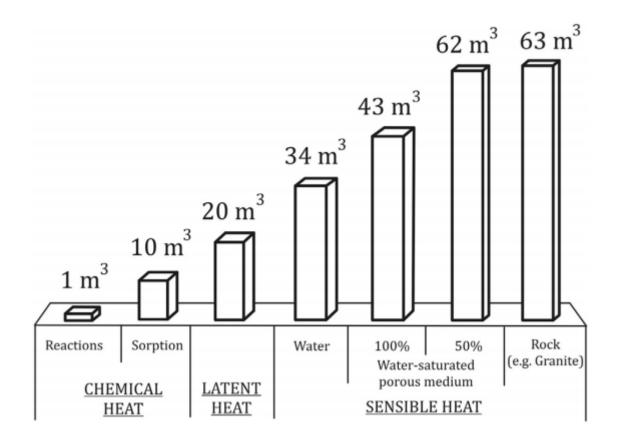


Figure 31. Volume needed to store 10 GJ with different storage mechanisms (N. Giordano, C. Comina, G. Mandrone and A. Cagni, 2015)

AB (liquid or solid) + heat
$$\Leftrightarrow$$
A (liquid or solid) + B (gaseous)
B (gaseous) \Leftrightarrow B (liquid) + heat

Figure 32. Sorption thermal storage system (B. Fumeya , R. Webera , P. Gantenbeinb , X. Daguenet-Frickb , T. Williamsonc , V. Dorera and J. Carmelieta, 2014)

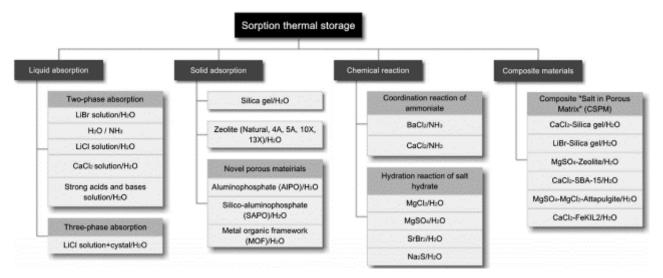


Figure 33. Sorption thermal storage classification (N. Yu, R.Z. Wang and L.W. Wang, 2013)

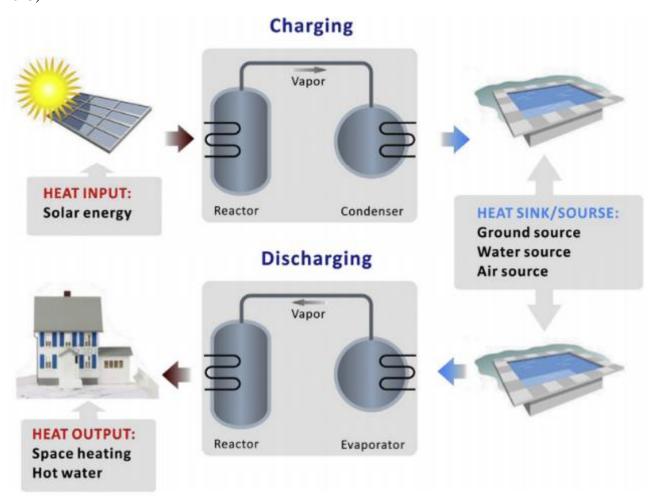


Figure 34. Operation principle of closed sorption thermal storage system (N. Yu, R.Z. Wang and L.W. Wang, 2013)

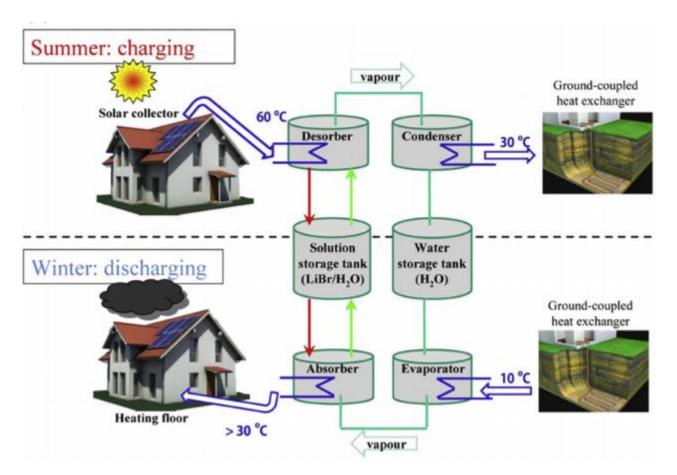


Figure 35. Long-term absorption storage cycle (N. Yu, R.Z. Wang and L.W. Wang, 2013)

As seen Fig. 31 the volume required to storage 1850 kWh (10 GJ*0.70/3600) of power. This has consideration of 30% heat losses and it has 70°C temperature increase in water. Other word volume needed to store 10 GJ with different storage mechanisms with a ΔT of 70°C. As shown sensible heat, storage takes lot more space than latent or chemical heat storage. That why it is better to storage in the underground. Underground storage is usually cheaper method to storage heat and more common way to store energy (N. Giordano , C. Comina, G. Mandrone and A. Cagni).

The long-term absorption storage cycle diagram shown in fig. 35. The top diagram is working principle in pressure-temperature-concentration and down one operation principle (N. Yu, R.Z. Wang and L.W. Wang, 2013). There sorption with work same

like Latent heat storage. In summer solar collectors, heat the sorption material so material gets desorbed and it condensed to ground source storage. Then in winter, it is happen opposite. The heat is slightly higher then outside in the winter ground source storage so first ground source storage heat evaporated with sorption material then vaporized and absorbed. Heat was release. That heat heats the house as seen Fig. 35 and Fig. 34. Every sorption materials have certain life cycle. That means it loses heat-storing efficiency. This system has been in the research and it is a new technology. In addition, it has good future.

3 RESULTS

3.1 Heat energy necessaries and economic impact

Heat energy necessaries in the northern countries are higher than tropical countries. This have affect in the economy too. As shown in Table.13, Finland use about 68% of their households energy consuming goes to heating of spaces. These storage systems are good candidate for Northern countries. This is large percentage of total households energy consumes by Finnish yearly. If it possible to get heating of space energy from renewable source. It would make positive impact in economic and environment. Top of that it will reduce the carbon footprint significantly. Other hand as seen Table 14 annual primary energy savings and is reduction in big time with aquifer thermal energy storage. The money is save by 71% and CO₂ emission is reduce by 73%. If the aquifer thermal energy storage lifetime is 40 years than the reduction of CO₂ will be significant.

Even though the ATES system economical cost is higher than conventional installation as seen Table 15. The overall ground source heat pump and solar thermal system have the best way get heat energy same way better human health maintain as seen Fig. 38. Greenhouse gas (GHG) has significantly reduces by solar thermal system, heat pump and biomass Fig. 36 renewable energies have row back that they are expensive investment but last thing should consider human health. Those investments are payback certain years later because of these are renewable energy and those are free fuel. For instance as seen Table 15 ATES system with heat pumps are payback time 8.4 years same time gas-fired boilers with cooling machines have 55000 € fuel cost every year but at same time ATES system with heat pumps is free of charge.

Table 13. Household energy consumption in Finland [GWh] (Statistics Finland, 2016)

	2010	2011	2012	2013	2014	2015
Heating of spaces	48 765	41 419	45 928	42 739	42 831	40 804
Residential buildings proper, total	46 365	39 339	43 663	40 643	40 690	38 760
- Detached houses	29 101	25 091	27 641	25 595	25 967	24 507
- Terraced houses	4 462	3 767	4 215	3 972	3 925	3 816
- Blocks of flats	12 802	10 481	11 807	11 076	10 798	10 437
Free-time residential buildings	2 399	2 080	2 265	2 097	2 140	2 044
Household appliances 1)	9 087	8 315	8 850	8 389	8 091	7 576
- Lighting	2 702	2 482	2 349	2 115	1 919	1 876
- Cooking	826	799	714	697	689	680
- Other electrical equipment	5 559	5 034	5 787	5 577	5 483	5 020
Heating of saunas	2 880	2 871	2 894	2 902	2 924	2 920
Heating of domestic water	9 522	9 584	9 658	9 727	9 789	9 850
Housing, total	70 254	62 189	67 330	63 757	63 635	61 150

 $\begin{tabular}{ll} \textbf{Table 14.} & Annual primary energy savings \& CO_2 emission reduction (D. Vanhoudt, J. Desmedt, J. Van Bael, N. Robeyn and H. Hoes, 2011) \\ \end{tabular}$

		ATES system + heat pumps (installation Klina)			Gas-fired boilers + cooling machines (reference-installation)				
	Unit	2003	2004	2005	Total	2003	2004	2005	Total
Electricity consumption	MWh _e	343	242	198	782	313	193	242	748
Gas consumption	GJ	0	0	0	0	6340	5739	4884	16,964
Primary energy consumption	GJ_p	4082	2878	2362	9323	12,350	10,104	9527	31,981
Reduction primary energy consumption	GJ₀ %	-8268 -67%	-7225 -72%	-7164 -75%	-22,658 -71%	-	-	-	-
CO ₂ -emissions	ton CO _{2eq}	211	149	122	483	681	561	525	1767
CO ₂ -emissions reduction	ton CO _{2eq}	469 -69%	412 -73%	403 -77%	1284 -73%	-	-	-	-

Table 15. Economic analysis with different systems (D. Vanhoudt, J. Desmedt, J. Van Bael, N. Robeyn and H. Hoes, 2011)

		ATES system + heat pumps (installation Klina)	Gas-fired boilers + cooling machine (reference-installation)
Investment costs	Underground installation (k€)	299	*
	Overground installation (k€)	266	241
	Heat exchangers	35	
	Pumps, ducts, appendages	46	
	Control equipment	116	
	Larger cooling coils	13	
	Frost protection cooling coils	32	
	Total installation costs (k€)	565	241
	Extra study and engineering costs for ATES installation (k€)	130	_
	Total, subsidies excluded (k€)	695	241
	Subsidies (k€)	244	-
	Total, subsidies included (k€)	451	241
Fuel costs	Cooling supply (MWh)	872	872
	Electricity consumption for cooling (MWh)	33	249
	Total cooling costs (k€)	3.7	27.4
	Heating supply (MWh)	1335	1335
	Gas consumption (MWh)	-	1571
	Gas costs for heating (k€)	<u>-</u>	55,0
	Electricity consumption for heating (MWh)	227	-
	Electricity costs (k€)	25.0	
	Total heating costs (k€)	25.0	55.0
	Total fuel costs (k€/year)	28.7	82.4
Simple payback time	Subsidies excluded (years)	8.4	
	Subsidies included (years)	3.9	

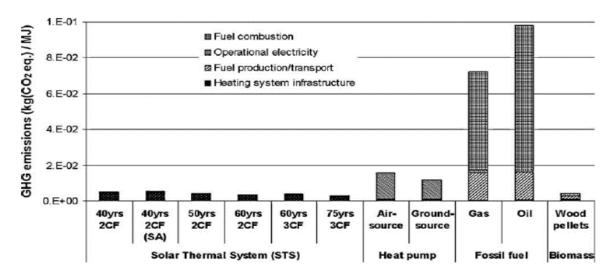


Figure 36. Life-cycle greenhouse gas (GHG) emissions (A. Simons, S. K. Firth, 2010)

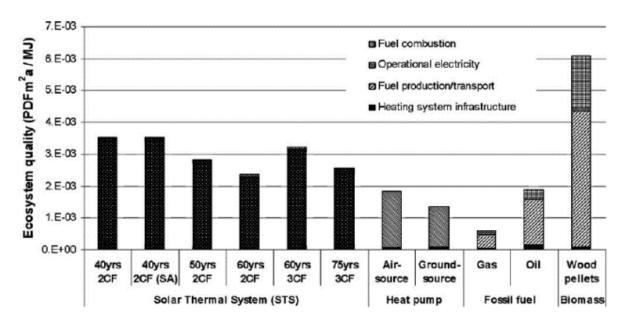


Figure 37. Potential impacts on ecosystem quality (A. Simons, S. K. Firth, 2010)

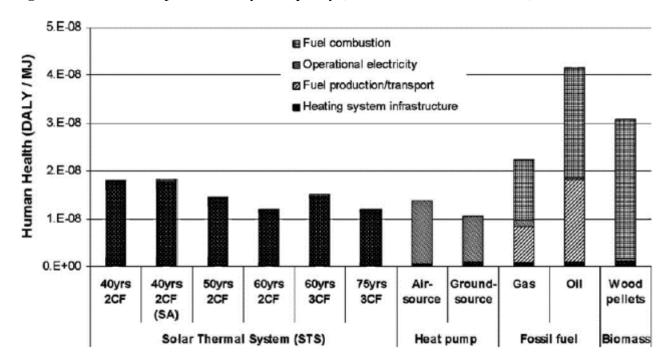


Figure 38. Potential impacts on human health (A. Simons, S. K. Firth, 2010)

Then comes life-cycle greenhouse gas (GHG) emission in solar thermal system has about 5 g/MJ of CO₂ and other hand fossil fuel has 90 g/MJ of CO₂ as seen Fig. 36. It is 18 times higher than solar thermal system. This data is showing clearly why renewable energy system is need in the future. Again, the human health inequality jumped significantly while using the fossil fuel as the energy source. For long-team, this could

be health problem for the people and will cost health care system big money as shown Fig. 38. According to the Andrew Simons and Steven K. Firth article, the problems such as carcinogens, respiratory organics, respiratory inorganics, climate change, radiation and ozone layer depletion are cause by use of fossil fuels.

Other hand when the businesses are going as right now for next 100 years then the atmospheric CO₂ concentrations will be 700 ppm. This is double the level of current level. In the preindustrial time, this was at the 280 ppm. The consequence of the rising CO₂ is temperature increase. It will increase by 3.5°C. This was happen last time 10000 years ago. Therefore, these systems will help to reduce the CO₂. In addition, other potential energy source system is combined heat and power (CHP) with borehole thermal energy storage. It has compared with just combined heat and power system and the result were big difference in carbon footprint. This is shown Fig. 39. This difference is showing the future potential of the combined heat and power with borehole thermal energy storage.

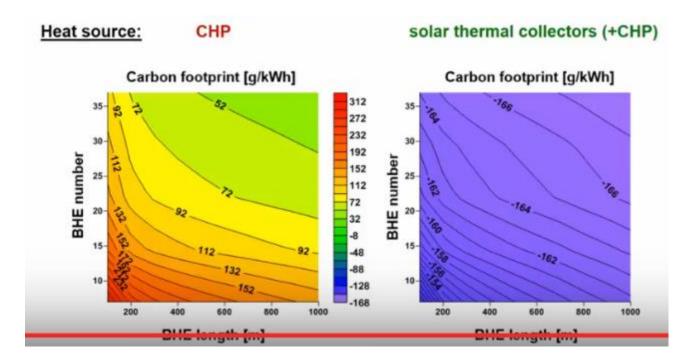


Figure 39. Carbon footprint (B. Welsch, 2015)

4 DISCUSSION

In order to discusses the advantages and disadvantages. First, the three different storage systems can be divide in to two systems. Those are sensible and phase changing thermal energy storages. The reason behind this decision is sorption and latent heat storage systems are sharing almost same principles. They are going through same processes. Phase changing thermal energy storage system have good future because of it can able to modify consumer's specification or climate sessions. All have to do mixing the different salts into the right percentage. It can mix with construction material and make the energy storing or it can part of the building itself as shown Fig. 29 and 30. Also phase changing thermal energy storage system didn't necessarily share a space. For instance, it could mix with window glass or cement and heat the room or cool the room with heat from sun only. Even though it is not so efficient in the cool Scandinavian countries but it works in the mild weather countries.

The main disadvantages are some of the materials environmentally not friendly, it could be expensive and production can produce lot of greenhouse gas emissions. Some of the phase changing salt is synthetic and these materials are mix with building material. Nowadays almost all the building materials are recycled when the build is demolished. If the synthetic salt inside the building material it could be harder or high energy is consuming to separate the partials. High energy means high CO₂ into atmosphere. To produce or to excavate the phase changing material need energy. Those places are mostly remote areas. It is difficult to get renewable energy do the excavation. Those places are dependent on Fossil fuel. This is again greenhouse gas emissions to the atmosphere. Electricity is most valuable energy all worlds consume. It cannot produce with these sensible and phase changing thermal energy storage systems.

The sensible thermal energy storage system has easy to install with low-tech solution to growing heat demand. It has most commonly in use and growing exponentially. Chine is count for 70% of the world sensible thermal energy user. In addition, it has been in use for every environmental condition. The system is mostly in the underground that means the outside weather affection did not or little impact to the system. It is hiding underground which is almost out of side and virtually takes no space. The down side is it needs big excavation. Big excavation is takes lot of fossil fuel consumes. Mostly it has to done in the basement of the building, which is only possible in the new building. There storage tanks are closed and sealed. It has difficulties to repair in the future damage. Of cause both their systems have big building cost comparing with traditional building. Starting cost may be big row back.

5 CONCLUSIONS

Thermal energy is good solution for greenhouse gas problem and ever-growing future energy need. The problem with this renewable energy storage starting cost is high. In order to get financing from banks are difficult. Better way to solving this problem is government financial help or getting tax deduction from them. At the same time, conventional energy producers (greenhouse gas emitters) have to pay carbon tax. This would be balance the financial burden from renewable energy producers.

These underground storages have less greenhouse gas emission but first have to dig big hole. Those underground storage holes or space digger uses diesel or other fuel to dick the hole or tank storage space. Those fuels did not put to the calculation. These storage systems have only heat energy storage. This heat energy to electricity production is difficult job.

Usually these storage systems are connecting to heat pump. Heat pump works with electricity and those are not cheap. Also heat pumps are expensive and short life expectancy then the storage tank or borehole components. Heat pumps are high maintains costs than conventional system. The electricity used in the heat pump usually comes with high carbon footprint. These entire problems can be or could be solved in the future because of the technology is developing in these sector.

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