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**Production and Testing
of Magnesium Carbonate
Hydrates for Thermal Energy
Storage (TES) Application**



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Born 1987

MSc Chemical Engineering (2015) from Åbo Akademi University, specialised in thermal energy storage by sorption and mineral carbonation processes.

Production and testing of magnesium carbonate hydrates for thermal energy storage (TES) application

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Preface

This thesis describes the production of magnesium carbonate hydrate (MCH) via a CO₂ mineralization process route developed at Åbo Akademi University (ÅA) and the testing of this material for thermal energy storage (TES) application. A TES reactor system was developed and tested using the MCH and a simulation model was developed for implementation of the system for the heating of houses or other buildings. Six journal papers report the findings.

The first two papers were a part of and funded by CLIC Oy CCSP project (2011–2016) (work package 5.2.2). Of several partners, primarily Nordkalk Ab Oy provided material and information for this work. CLIC Oy was funded by Finnish Funding Agency for Technology and Innovation, Tekes and several program partners.

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This thesis was written under supervision from Professor Ron Zevenhoven, giving valuable support during the studies and research. He introduced me to the field of carbon capture and was always helpful at every stage of the work.

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Finally, I want to thank my wife Helena support during this time and my children Elias and Milou for and helping me stay motivated. Helena has always stayed positive during sometimes stressful times.

Svensk sammanfattning

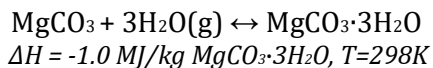
I denna avhandling ingår både forskning inom koldioxidavskiljning och lagring genom mineralisering (CCSM) (carbon capture and storage by mineralisation, CCSM) och produktion av dess slutprodukt, magnesiumkarbonathydrat (MCH) för lagring av termisk energi (thermal energy storage, TES). Senare delen av avhandlingen behandlar utvecklingen av en process som använder MCH som ett TES-material inklusive termisk systemmodellering och simulering med hjälp av de experimentella resultaten.

För att uppnå målen i Parisavtalet (Förenta nationernas klimatavtal) om minskade koldioxidutsläpp är alla fungerande och genomförbara åtgärder viktiga, inklusive teknik för förnybar energi och koldioxidavskiljning och lagring (CCS). Utgående från det faktum att geologisk koldioxidlagring inte är möjlig i Östersjön, är CCSM Finlands ända CCS alternativ. CCS (och CCSM) är mycket forskat runt om i världen och vid Åbo Akademi har en magnesiumbaserad CCSM-process utvecklats (kallas ÅA-route).

TES kan utöka användningen av värme som produceras i förnybara källor som inte tillgodoser efterfrågan på en gång. Genom att utveckla ett material av CCSM-karbonatprodukten som förmodligen finns tillgängligt i rikliga mängder i framtiden, motiverar CCSM ur både ekonomisk och miljömässig synvinkel. Avhandlingen är en del av fortsättning på forskningen av tidigare arbete med CCSM-processen (ÅA-route), som utvecklats vid Åbo Akademi. I de två första artiklarna rapporteras arbetet kring möjligheten att hitta lämpliga mineraler (rest mineral eller anrikningssand) närmare industrin med rikliga CO₂-utsläpp i Finland. Det är uppenbart att energianvändningen och koldioxidutsläppen för CCSM-processen bör minimeras (transportsträcka och kemisk effektivitet vid extraktion). I artiklarna jämförs magnesiumutvinning från två serpentinitmineraler, Mg-hornblende och diopsid från fyndigheter i Finland. Studien jämför två extraktionsprocesser av magnesium (fastfas / fastfas, 440 ° C och vätskefas / fastfas 70-100 ° C) för dessa mineraler, samt föreslår nya proportioner och blandningar av extraktionssalter.

De bästa extraktionsresultaten i studien med en vätskefas / fastfas reaktor ger en CO₂-bindningskapacitet på 292 kg CO₂ / ton (Serp-A 500 km från CO₂-källan) eller 260 CO₂ / ton (Serp-B, 100 km från CO₂-källan). Däremot skulle en fastfas / fastfas reaktor binda 240 kg CO₂ / ton och 207 CO₂ / ton. Denna studie sammanfattar de olika fördelarna med båda metoderna. Beslut om det mest fördelaktiga processalternativet kan göras utgående från möjligheterna från fall till fall (t.ex. spillvärmtemperaturer). CCSM-processen (ÅA-route) producerar magnesiumkarbonat (vattenfri och trycksatt karbonatisering) och magnesiumkarbonathydrat (MCH, karbonatisering i vätskelösning). Beroende på förhållandena kan MCH falla ut som nesquehonite, lansfordite och

hydromagnesit. Nesquehonite desorberar kristallvatten och bildar magnesiumkarbonat enligt reaktionen nedan, vilket ger en värmeeffekt som är tillräcklig för lagring av termisk energi:



Denna reaktion har betydligt lägre driftstemperaturer än de flesta andra kemiska abs-/adsorberande material och salter. Utöver denna fördel, fungerar MCH även som brandskyddsmedel. Desorptions- / dehydratiserings-temperaturerna är 60-70 °C, och adsorption / hydratisering är möjlig vid temperaturområdet 5-25 °C. Denna studie föreslår dock att materialet bör blandas med kiselgel för tillräcklig kinetik.

Värmelagring genom abs-/adsorption går ut på att använda sol (eller annan förnybar värmekälla) för att värma upp det absorberande materialet under sommaren där energi kan släppas ut (hydratisering) under vintern. I denna studie presenteras två olika koncept. Det första är ett slutet TES-system var berg-/jordvärme används som energikälla för att generera vattenånga. Det andra konceptet är ett öppet TES-system där vattenånga från inomhusluften utnyttjas. Det öppna TES-systemet visade sig vara mera fördelaktigt och valdes för vidare studier.

Kompositmaterialet som utvecklades i denna studie, blandad nesquehonite (NQ) och kiselgel (SG), abs-/adsorberar vattenånga effektivt vid hög (75%) relativ luftfuktighet, men betydligt sämre vid låg relativ fuktighet (25-50%). Dessa resultat erhöles vid laboratorietest med små prov på några gram bestående av granuler på 3-5 mm. Maximal värmekapacitet som kunde erhållas med detta material var 0,7 MJ/kg vid 25 °C och 0,36 MJ/kg vid cirka 5 °C. Konceptet med öppet TES-systemet är baserat på en frånluftsvärmepump som sänker utloppstemperaturen (från inomhusluften) för att öka relativa fuktigheten. I syfte för att testa konceptet, byggdes en laborariepilot för testning av konceptets prestanda. Med detta (större) system erhöles en värmekapacitet på 0,41 MJ/kg vid 25 °C och 0,29 MJ/kg vid cirka 5 °C.

Reaktionshastighetsdata erhållna från laborariepiloten användes i en simuleringsstudie av konceptet. I simuleringarna analyserades möjligheten (samt effektiviteten) att ersätta elektrisk motståndsvärme med TES-reaktors värme (för att stödja värmepumpen) under vinterhalvåret. Det visade sig att cirka 70% av elektriska värmen var möjlig att ersätta med TES, som innehåller MCH + kiselgel. Dessutom förbättrar systemet också ventilationsvärmväxlarens prestanda genom att eliminera frysproblemet på grund av torkad utloppsluft.

Abstract

This thesis covers both research of carbon capture and storage by a mineralisation (CCSM) process and production and use of the end product, magnesium carbonate hydrate (MCH) for thermal energy storage (TES). The development of a process using MCH as a TES material includes thermal system modelling and simulations using the experimental results.

To reach the goals of the Paris climate agreement on reduced CO₂ emissions, all feasible measures are important, including renewable energy technologies and carbon capture and storage (CCS) technologies. Considering that geological CO₂ storage in Finland or the Baltic Sea region is not possible, the only option in/near Finland is CCSM. CCS (and CCSM) is broadly investigated around the world, and a set of magnesium silicate -based CCSM processes have been developed at Åbo Akademi University (referred to as ÅA-routes). (Often CCSM is classified as carbon capture and utilization, CCU.)

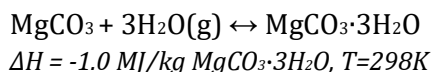
TES can expand the use of heat produced by renewable sources that do not meet the demand at the same moment. Developing a material out of the CCSM carbonate product that is useful in the future motivates CCSM from both economical and environmental points of view.

The thesis is a continuation of the earlier research on the CCSM process (ÅA routes) developed at Åbo Akademi University. The first two papers study the possibility to find suitable rock (for example mining tailings or overburden) closer to the CO₂ emitting industry (in Finland). It is obvious that the energy use and CO₂-emissions for the CCSM process should be minimized. Magnesium extraction from two serpentine mineral containing rock, a Mg-hornblende and a diopside found in Finland are compared.

The study compares solid/solid (440 °C) and aqueous/solid extraction (70-100 °C) from these rocks and suggests new mixtures of extraction salts . (Once extracted, the downstream carbonation conversion of the magnesium can be assumed to be > 90%.) The best extraction results with an aqueous/solid reaction would have CO₂ binding capacity of 292 kg CO₂/ton (Serp-A 500km from the CO₂-source) and 260 CO₂/ton (Serp-B, 100km from the CO₂ source), while the solid/solid reaction would allow for binding 240 kg CO₂/ton and 207 CO₂/ton, respectively. This study determines the advantages of both methods although the selection of the most feasible process alternative needs to be done depending on the CO₂ emitting process (eg. waste heat temperatures) and its location.

The CCSM process (ÅA route) produces magnesium carbonate, magnesite (via dry, pressured carbonation) and magnesium carbonate hydrate , MCH, (via wet carbonation). Depending on the conditions nesquehonite, lansfordite and hydromagnesite may be formed. Nesquehonite can desorb its crystal water and

form magnesium carbonate according to the reaction below, giving a heat effect sufficient for significant thermal energy storage:



Compared to most of the other chemical sorption compounds, its advantages are low operating temperatures for TES while it can in case of emergency act as a fire retardant. The desorption/dehydration temperatures are 60-70 °C, and adsorption/hydration is possible at the temperature range of 5-25 °C. However, our studies suggests that the material should be mixed with silica gel for sufficiently fast reaction kinetics.

The basic procedure is using solar heat (or other heat source) for heating up the sorbent material during summertime after which energy can be discharged (hydration) during winter. Two concepts were presented, a closed TES system using geothermal heat for water vapour generation and an open TES system using water vapour from indoor air, respectively. The open TES system was chosen for further system studies.

The composite material, a 50%/50% weight mixed nesquehonite (NQ) and silica gel (SG), efficiently chemisorbs water vapour at high (75%) relative humidity (RH) but sorption at low RH (25–50%) RH is compromised. The samples being small (3-5mm) granules, and the best heat capacity obtained of the chemisorption reaction was 0.7 MJ/kg at 25 °C and 0.36 MJ/kg at around 5 °C.

The open TES system suggested is based on an exhaust air heat pump decreasing the outlet (from indoors) the air temperature as to increase the RH. For this, a laboratory pilot for testing the concept performance was built. Using this larger system a heat capacity of 0.41 MJ/kg at 25 °C and 0.29 MJ/kg at around 5 °C were obtained. The reaction rate data obtained was used in simulations based on the concept. The performance of using the TES reactor to supply heat instead of electrical resistance heat (to support the heat pump) in the winter was analysed. Around 70% of the otherwise needed electrical resistance heat may be substituted for with TES using MCH + silica gel. As a side-benefit, the system also improves the performance of the ventilations heat exchanger by eliminating the freezing issue by drying the exhaust air.

Contribution of the author and list of publications

The author of this thesis carried out most or all the experimental work and/or simulation model development and testing as reported in Papers II-VI. He also supported the writing of Paper I where the methods used in Papers I and II are compared.

- I. KOIVISTO, E., **ERLUND, R.**, FAGERHOLM, M. and ZEVENHOVEN, R. (2016). Extraction of magnesium from four Finnish magnesium silicate rocks for CO₂ mineralisation -Part 1: Thermal solid/solid extraction. *Hydrometallurgy*, 166, 222-228.
- II. **ERLUND, R.**, KOIVISTO, E., FAGERHOLM, M. and ZEVENHOVEN, R. (2016). Extraction of magnesium from four Finnish magnesium silicate rocks for CO₂ mineralisation -Part 2: Aqueous solution extraction. *Hydrometallurgy*, 166, 229-236.
- III. **ERLUND, R.**, ZEVENHOVEN, R. (2017). Thermal storage of (solar) energy by sorption of water in magnesium (hydro) carbonates, *International Journal of Thermodynamics*, 20(2), 102-109 open source
- IV. **ERLUND, R.**, ZEVENHOVEN, R. (2018). Hydration of magnesium carbonate in a thermal energy storage process and its heating application design. *Energies*, 11, 170 open source
- V. **ERLUND, R.**, ZEVENHOVEN, R. (2019), Thermal energy storage (TES) capacity of a lab scale magnesium hydro carbonates/silica gel system, *Journal of Energy Storage*, 25, 100907
- VI. **ERLUND, R.**, ZEVENHOVEN, R. (2020), Simulations on design and system performance of building heating boosted by thermal energy storage (TES) with magnesium hydro carbonates/silica gel, *Energies*, 13(17) 4520 open source

Related publications

- ZEVENHOVEN, R., SLOTTE, M., KOIVISTO, E. and **ERLUND, R.** (2017). Serpentine carbonation process routes and integration in industry. *Energy Technology* 5(6), 945-954 (open access)
- ZEVENHOVEN, R., SLOTTE, M., KOIVISTO, E. and **ERLUND, R.** (2018). Serpentine carbonation using the Åbo Akademi routes – status update. Presented (by RZ) at ACEME2018, Newcastle NSW, Australia, March 10-14, 2018.
- ZEVENHOVEN, R., **ERLUND, R.**, TVEIT, T-M. (2019). Energy efficiency of exhaust air heat recovery while controlling building air humidity: A case study, *Energy Conversion and Management*, 195, 1238-1243

CLIC Oy CCSP deliverables

- D548. 2015. **ERLUND, R.**, KOIVISTO, E., MATTILA, H.-P., ZEVENHOVEN, R. and FAGERHOLM, M. Process for upgrading diopside-based rock for lime kiln gas CO₂ carbonation. Deliverable; CLEEN CCSP WP5.2.2.
- D555. 2016. KOIVISTO, E., **ERLUND, R.**, ZEVENHOVEN, R. and FAGERHOLM, M. Extraction of magnesium from four Finnish magnesium silicate rocks for CO₂ mineralisation. Deliverable; CLIC Innovation Oy Carbon Capture and Storage Program (CCSP).
- D556. 2016. ZEVENHOVEN, R., KOIVISTO, E., **ERLUND, R.**, SLOTTE, M. and FAGERHOLM, M. Updated cost evaluation including a feasible plant design for large-scale magnesium silicate carbonation at a lime kiln. Deliverable; CLIC Innovation Oy Carbon Capture and Storage Program (CCSP).

List of abbreviations and symbols

ABS	Ammonium sulphate
AS	Ammonium bisulphate
CCS	Carbon capture and storage
CCSM	Carbon capture and storage by mineralisation
COP	Coefficient of performance
DG	Dypingite
DNQ	Dehydrated nesquehonite
EAHP	Exhaust air heat pump
EDAX	Energy-dispersive X-ray
ERH	Electrical resistance heat
ΔH	Chemical capacity (kWh)
HRV	Heat recovery ventilation
$\Delta m/m$	Mass increase per dehydrated reactor material (g/g _{sample})
LCA	Life cycle assessment
MCH	Magnesium carbonate hydrate
NQ	Nesquehonite
OU(n)	Operating unit and its order number n
Q_{TES}	Total reactor heat output from the TES reactor (kW)
R(n)	Reactor unit and its order number n
RH	Relative humidity
Serp – A	Serpentine located 500km from CO ₂ -emission unit location
Serp – B	Serpentine located 100km from CO ₂ -emission unit location
SG	Silica gel
SH	Specific humidity (kg moisture/kg air)
STES	Seasonal thermal energy storage
T_{dew}	Dewpoint temperature (°C)
TES	Thermal energy storage
z	see $\Delta m/m$

Table of Contents

Preface.....	i
Svensk sammanfattning	ii
Abstract.....	iv
Contribution of the author and list of publications.....	vi
<i>Related publications</i>	vii
CLIC Oy CCSP deliverables.....	vii
List of abbreviations and symbols	viii
1. Introduction.....	1
1.1 Carbon Capture Storage by mineralization (CCSM).....	2
1.1.1 Magnesium based CCSM	2
1.1.2 ÅA-routes for serpentinite rock carbonation	2
1.1.3 ÅA-route variations.....	3
1.2. Production of magnesium carbonate hydrate (MCH)	6
1.3 Thermal energy storage (TES)	7
1.3.1. Sensible heat storage	8
1.3.2. Reversible chemical reactions.....	8
1.3.3. Latent heat storage.....	8
1.3.4. TES by sorption	8
1.3.5. Reactor systems – TES by sorption.....	11
2. Aim of the research / research questions.....	13
3. Magnesium extraction from silicate rock: materials and methods (Paper I – II).....	14
3.1 Solid/solid and aqueous/solid extraction.....	15
4. Material properties and development	16
4.1 Magnesium carbonate hydrate (MCH)	16
4.2 Hydration –initial tests of MCH.....	16
4.2.1. MCH - silica gel mixtures (Paper III)	17
4.2.2. Production of nesquehonite (NQ) and preparations of composite material	17
4.2.3 Sorption in a closed system TES Concept (Paper IV).....	18
4.3 Dehydration.....	19
4.4 Material analysis – aging, cycling.....	21
4.4.1. Thermogravimetric analysis	22

5. Process systems and simulations	25
5.1 STES Open reactor systems and relative humidity (RH)	25
5.2. The concept - Open reactor coupled with an exhaust air heat pump (EAHP)	25
5.3. Set-up for concept testing (kinetics and enthalpy) (Paper V)	29
6. Key Findings.....	32
6.1. Extraction (Paper I – II).....	32
6.2 Hydration / Chemisorption results (Paper III, IV, V).....	35
6.2.1 Water vapour sources	36
6.2.2 Hydration kinetics, heat rate and serial reactor configurations (Paper V and VI)	37
6.3 Simulations and concept system limitations.....	39
7. Conclusions	45
7.1 Magnesium extraction from rock	45
7.2 Seasonal thermal energy storage with magnesium carbonate hydrate.....	45
7.3. Future work.....	47
References	48

1. Introduction

To reach the goals of the Paris climate agreement on reduced CO₂ emissions, several studies suggest that both renewable energy technologies and carbon capture and storage (CCS) technologies have to be applied on a larger scale. Biofuels and hydropower plants can be used on demand, although biofuel-fired power plants are usually designed to run most of the time. Solar power and heat can meet demands during daytime at sunny parts of the world but at locations further from the equator the sunlight varies more with the season. This requires sufficient energy (heat and electricity) storage both for day/night and longer, seasonal periods. The stability of wind power delivery varies very much with location, which may result in an electricity and/or thermal energy storage (TES) demand. Both wind and solar largely exceed the energy demand during certain periods, and long time storages such as eg. hydrogen gas or seasonal heat storage (in colder regions) will become increasingly important and might solve the supply problems.

The absence of underground CO₂ storage capacity in Finland (and many other countries) for “conventional” carbon capture and storage (CCS) that involves underground storage (EC, 2009), makes the alternative mineral carbonation, or CO₂ mineralisation, more interesting. Absorbing flue gas CO₂ into aqueous solution and precipitating carbonate containing minerals can give more favourable opportunities for the long-term storage of large amounts of CO₂, with a capacity much larger than what “conventional” CCS may offer (Lackner 2003, Zevenhoven et al. 2016).

As one ton of CO₂ will result in several tons of carbonate (and other solid) product there is a strong need for a purpose and preferably high economic value application of these materials. Application as a thermal energy storage (TES) material for low temperature applications was recognised and investigated at ÅA since 2016, while interest of TES in Finland is increasing.

This thesis covers both the CCSM processes for producing a magnesium carbonate hydrate (MCH) and the development of a process that uses it as a TES material, including thermal system modelling using the experimental results.

The thesis is a continuation of earlier work on the CCSM process developed at Åbo Akademi University that resulted in doctor theses of Nduagu (2012) and Fagerlund (2012) followed by Romão (2015), Lavikko (2017), Slotte (2017) and Koivisto (2019) and the MSc theses of Björklöf (2010) and Åbacka (2013), amongst others. The two first papers (I-II) address more directly the CCSM process and the later papers (III-VI) describe the development of the

TES material product and TES heating concept and simulation of its use in a technical system.

1.1 Carbon Capture Storage by mineralization (CCSM)

1.1.1 Magnesium based CCSM

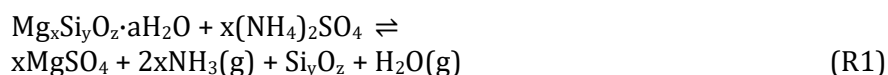
Magnesium can be extracted more or less efficiently from various types of minerals as present in rock and industrial wastes (Styles et al. 2014). Mining rock for CCSM purpose is often unnecessary, as in many places in Finland and elsewhere large amounts of tailings of serpentinite are piling up (Teir et al. 2007). Using mining tailings is more economical than mining rock specifically for CCSM, saving energy which is an obvious advantage regarding CO₂ utilization.

1.1.2 ÅA-routes for serpentinite rock carbonation

A magnesium based CCSM process (including some variations) has been developed at Åbo Akademi University (referred to as ÅA-routes).

The ÅA-routes provide two options for the first step of the process, i.e. extraction of magnesium from the silicate mineral. These two options or methods are compared in this thesis, in article (appended papers) I and II. Thermal solid/solid extraction has been tested by several other authors, and it was compared to extraction in aqueous solution. However, another objective of the study was testing the extraction performance for four Finnish magnesium silicate-containing rock.

The reactor used for this process step (a lab-scale rotary kiln) is heated to around 440 °C in the thermal extraction method, allowing the magnesium in the grinded silicate rock (size of the order 0.1-0.2 mm) to react with ammonium sulphate (AS) (may be mixed with ammonium bisulphate, ABS) according to reaction R1. A part of the ammonia vaporises and sulphate forms bisulphate according to reaction R2. The presence of liquid water in the reactor does somewhat increase the heating energy but may give better magnesium extraction. Afterwards the material is cooled and put in water mainly resulting in dissolved MgSO₄, NH₄(SO₄)₂ and NH₄HSO₄, iron and calcium and solid silica and unreacted mineral residue. (Romao et al. 2013). As shown by Nduagu et al. (2014), no sulphur oxide vapours are produced during this step.





The other option, aqueous extraction, uses an acidic ABS mixed with AS solution for extraction the magnesium. The bisulphate ion is a weak acid, gives considerably more H^+ ions (see reaction R3 and R4) than the ammonia ion giving a pH value around 1.5 with 0.7M AS and 0.7M ABS. Paper II of this thesis showed that the use of ABS alone (Wang and Maroto-Valer, 2011) is not needed: a mixture of AS and ABS is effective too.



The aqueous extraction of magnesium is still suitable and efficient for minerals such as olivine, which will however not react as efficiently with AS as in the thermal solid/solid reactor (Styles et al. 2014). However, serpentines are more common and widespread and are also easier to pulverise and grind (Teir et al. 2007).

The CO_2 emissions from electricity production is generally in the order of 300 – 800 g / kWh depending on the fuel, which is around 80 to 220 g CO_2 per MJ. However, CO_2 is produced during iron- and steelmaking, petro (chemical) processing and cement/lime production to name a few. The ÅA-routes requires heat and electricity depending on the process route chosen, which depends on CO_2 concentration in the flue gas to be processed and the availability of (waste) heat for the extraction of magnesium from suitable (preferably serpentinite) rock.

According to Zevenhoven et al. (2016) the energy input requirements vary from 0.9 + 2.6 MJ/kg CO_2 electricity + heat, respectively, to 0 + 15.4 MJ/kg CO_2 , for fixation into carbonate. Modern methods for recovery of the ammonium (bi)sulphate flux salt based on ion-selective and bipolar membranes bring down the energy penalty (Koivisto, 2019, Zevenhoven and Häggqvist, 2021).

1.1.3 ÅA-route variations

The first option (1) is shown in Figure 1a, extracting the magnesium with the thermal solid/solid method. The extraction produces magnesium sulphate which in aqueous solution at $\text{pH} > 10$ forms magnesium hydroxide, which is precipitated, after adding the ammonia vapour (NH_3) released from the extraction phase (Nduagu 2012). The magnesium hydroxide is carbonated in a pressurised fluidised bed, at 500 °C, 20 bar CO_2 (Fagerlund 2012). The carbonation step produces a large part of the heat needed for the thermal step upstream.

However, given the complexity of the carbonation step in option 1, another carbonation option was developed which is less complex but less energy-efficient too. In the second option (2) precipitation and carbonation are combined in an aqueous solution reactor (Figure 1b). The CO_2 rich flue gas is absorbed in the solution and addition of recycled ammonia will result in precipitated magnesium carbonate hydrate (MCH). The reaction is further discussed below (section 1.2). The third option (shown in Figure 1c) differs from the second option by using ABS for extraction which is separated from the first aqueous solution after the extraction using an anion-selective membrane that separates SO_4^{2-} ions from HSO_4^- ions. Note that, for the extraction step both thermal solid/solid (1c) or aqueous/solid (1d) described above can be implemented as given in Paper I and II. The membrane separations involved have been studied by Koivisto (2019).

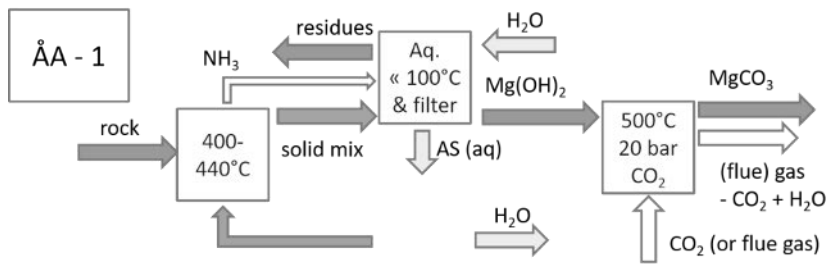


Figure 1a – Process scheme of conventional ÅA route, option 1 (Zevenhoven et al. 2017)

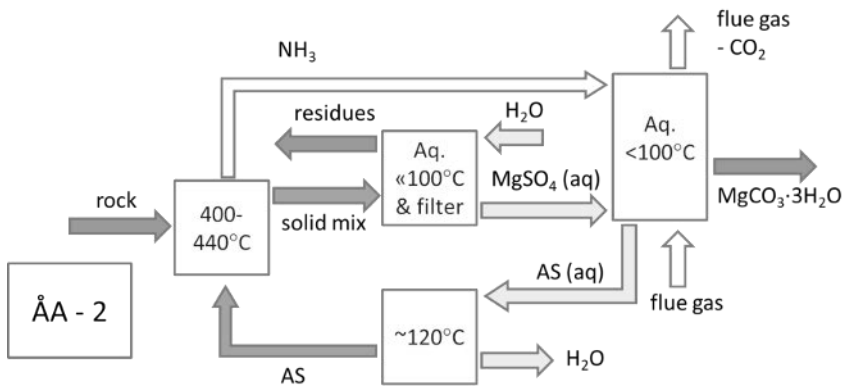


Figure 1b – Process scheme of ÅA route option 2 (Zevenhoven et al. 2017)

1. INTRODUCTION

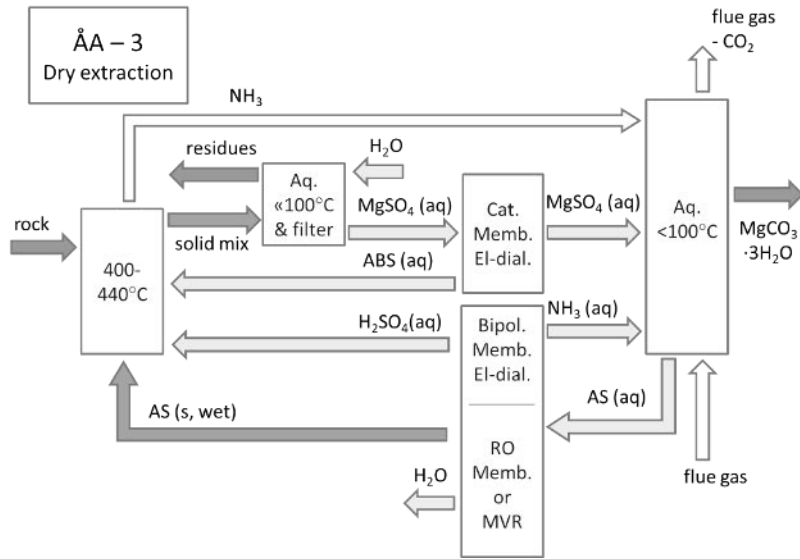


Figure 1c – Process scheme of ÅA route option 3 with dry extraction (picture by R. Zevenhoven 2020)

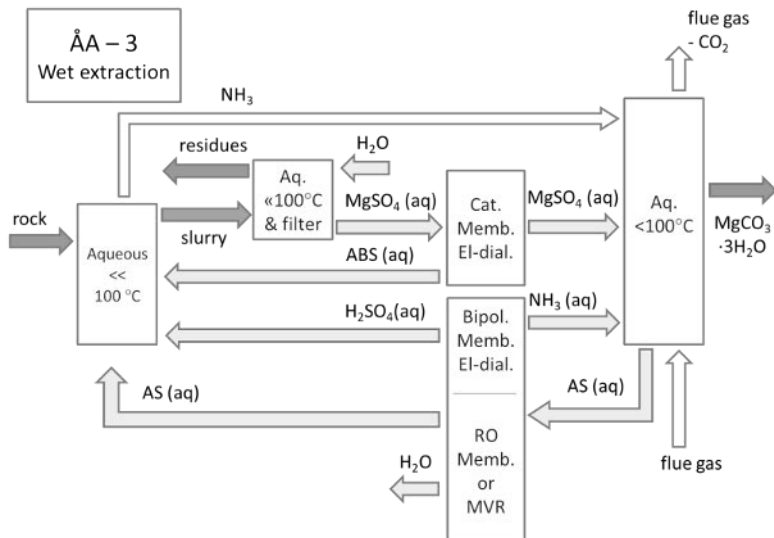


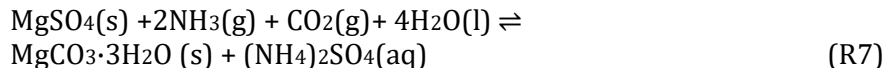
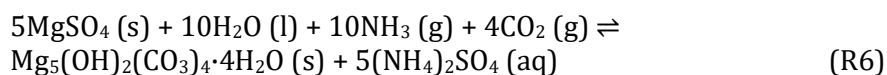
Figure 1d – Process scheme of ÅA route option 3 with wet extraction. (picture by R. Zevenhoven 2020)

1.2. Production of magnesium carbonate hydrate (MCH)

As mentioned earlier, magnesium carbonate can be produced via mineral carbonation with several methods using MgSO_4 from the extraction. Pure magnesium carbonate can be produced with the conventional ÅA-route (option 1) (Fagerlund 2012, Nduagu 2012).

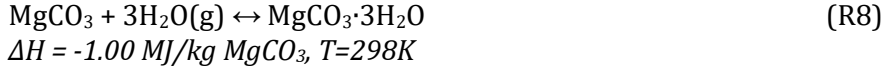
The production via aqueous precipitation (ÅA-route option 2 and 3) results in a variety of crystals of magnesium carbonate hydrate (MCH) as nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), landsfordite ($\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$), hydromagnesite ($\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$) and dypognite (Teir et al. 2007, Hill et al. 1979, Jauffret et al. 2015).

The precipitation of MCH in aqueous solution gives products depending on the temperature and the amount of absorbed CO_2 . Generally, nesquehonite (NQ) precipitates (according to reaction R6) between 30 °C and 0.01 bar CO_2 to 50 °C and 1 bar CO_2 . Above 50 °C hydromagnesite (HM) starts to precipitate (shown in reaction R7) (Zevenhoven et al. 2016). A more detailed description of the production NQ can be found in paper III.



Moreover, too low concentrations and a temperature below 50 °C may result in HM precipitations (Morrison et al. 2016). Noticeable is that the HM contains four carbonates CO_2 per five magnesium atoms compared to nesquehonite (and magnesite), containing 1:1 bound CO_2 to Mg. Studies have shown that nesquehonite can degrade to hydromagnesite at high temperatures (above around 50 °C) with time, but results are varying (Jauffret et al. 2015, Hull et al. 2011). Another advantage with NQ is the applicability for various products, as building materials and thermal energy storage, but very large markets for this are yet to be developed

Studies by others shows that the NQ crystal can be used in building materials and blocks with a similar strength as gypsum. It is produced by mixing the NQ with water and pressing (and drying) the mixture into a block, giving the NQ a more or less agglomerated or ill-crystalized phase called "phase X" (Glasser et al. 2016). Magnesium carbonate hydrate in form of NQ can store heat by desorbing crystal water (charge thermal energy) and by sorption of water vapour (discharge thermal energy).



Moreover, to obtain sufficient kinetics, in this work NQ was mixed with silica gel (SG) forming composite material for thermal energy storage (TES). The theoretical heat capacity for NQ is 1.00 MJ/kg and 0.62 MJ/kg for silica gel, which is 6, respectively 3.5, times more energy dense than storing heat in water.

Full-scale CCSM processes capturing large amounts CO₂ may produce MCH in abundant amounts. Developing any useful (with market value) MCH product would be beneficial, to avoid costs for storage of it. Obviously, using it as aggregates for soil filling would be a simple solution to avoid costs, while little value would be created. However, a useful solution for the MCH material would support the feasibility and favourably of CCSM, which is the main motivation for this study besides producing a low cost material for thermal energy storage.

1.3 Thermal energy storage (TES)

One of the main challenges for reducing CO₂ emissions and having a renewable energy system is the heat demand in the winter in the colder parts of the world. Renewable sources like hydropower and biofuels can provide energy on demand but both of them have limitations. Wind power is challenging to predict for longer periods and presumably is not the answer without extensive electricity or hydrogen storage, which however is rather expensive. Solar power and heat are seasonally limited and usually the capacity is exceeding the demand in the summer. Solar heating is an efficient and low cost energy source and the heat demand is largest in the winter. Extensive solar heat storage (or thermal energy storage, TES) for use in the winter decreases the demand for heating capacity in the winter, referred to as seasonal thermal energy storage (STES). Depending on the regions level of investment in renewable energy sources, STES decreases the number of coal, oil or gas power plants required during the winter. Alternatively, the STES would decrease the required capacity of non-fossil power plants using biofuels, or hydropower or nuclear power plants, being a possible advantage as these investments are very high in many cases. The relatively simple technology allows for STES to be installed locally, decreasing the capacity demand and complexity of grid systems (incl. electrical storage) following more extensive use of renewable such as wind and solar power, zero-

emissions electricity. Nonetheless, the development and implementation of TES and electricity storage must go in parallel.

1.3.1. Sensible heat storage

Conventional or sensible large-scale seasonal thermal energy storages, such as water, gravel, rock etc. usually require very large volumes and is associated with significant heat losses. Studies show that large underground storage water tanks (and water-gravel) have an annual average 60% efficiency (re-use of stored energy) (Bauer et al. 2010).

1.3.2. Reversible chemical reactions.

At high temperatures reversible chemical reactions for storage give the highest energy density. The temperature required for heat sources is around 200–1000 °C (N'Tsoukpoe et al. 2009).

1.3.3. Latent heat storage

Phase changing materials (PCM) can be an option for TES, belonging to the latent heat storage group, typically organic materials or salt melting processes. Paraffin wax can provide 174.4 kJ/kg with a high density (1840 kg/m³) however, only 40% efficiency was obtained (Aydin et. al, 2015). Another material, a microstructured polyol(erythritol)–polystyrene composite using high internal phase emulsion polymerisation, gave a TES capacity 0.33 MJ/kg at 115-120 and 0.2 MJ/kg at 0–50 °C melting/crystallisation temperatures (Puupponen et al. 2016). Storage of the material over 30 days above 5°C reduces the heat content, decreasing its long term storage possibilities (Turunen et al. 2020). Moreover, it could be mentioned that these numbers can be matched by the far more economical sensible heat storage (see Figure 2) depending on the temperature of the heat source ($\Delta T_{\text{water}} = 40^{\circ}\text{C}$: 0.17 MJ/kg and $\Delta T_{\text{water}} = 80^{\circ}\text{C}$: 0.34 MJ/kg).

1.3.4. TES by sorption

Amongst the other types listed above, TES by sorption is a widely studied and several materials have been tested during the last two decades. The sorption process has no heat losses when it is not in use/required, increasing the STES efficiency. The sorption media can be shut/throttled, and no chemical reaction or heat conduction will appear as would with latent or sensible heat storage, respectively.

The material considered most promising and suitable from physical point of view for TES is usually zeolite. Studies show that zeolite can store up to 1.0

MJ/kg heat and requires 100-140 °C for dehydration, releasing water vapour. Both heat storage capacity and dehydration temperatures vary depending on the zeolite type (Whiting et al. 2013).

Several materials studied for TES are listed in Table 1. Considering heat transfer issues above water's boiling point and that high temperatures with solar collectors requires very strong solar radiation, which may last for a limited time only, zeolite configurations requiring around 100°C seem preferable. The work described here, however, focusses on temperatures <100°C where requirements are highest especially for private households and office and municipality buildings.

The material price is rather high for zeolites and recent studies show that TES using zeolites has a payback time of over 30 years (Mahon et al. 2020). Other affordable materials (mainly salts) are interesting for this purpose, and are widely studied: MgSO_4 , MgCl_2 and CaCl_2 to name a few.

MgSO_4 can adsorb a large amount of water vapour in relation to its dry mass, resulting theoretically (see Figure 2) in up to 1.74 MJ/kg TES capacity and up to seven crystal water molecules per salt molecule (van Essen et al. 2008). Studies where it is combined or mixed with zeolite 13X, to increase the TES capacity of zeolite, showed the opposite effect. More importantly, initial hydration of MgSO_4 forms thin impenetrable crust on the particle, blocking further water vapour absorption (Hongois et al. 2011, Whiting et al. 2013). However, optimal use was shown by others that mixing zeolite and MgSO_4 can improve the TES capacity, still partly blocking the water absorption capacity of zeolite. Studies showed that around 30% of a heating system can be substituted for with this TES material (Mohan et al. 2020).

Zondag et al.'s studies showed that by sorption of water by MgCl_2 ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$) could give a storage capacity of 0.5 GJ/m³ in a packed bed with 50% porosity. Theoretically the reaction enthalpy would allow for 2 GJ/m³ (around 0.9 MJ/kg, with bulk density 2320 kg/m³ for MgCl_2), and around 1 GJ/m³ with the porosity mentioned (Zondag et al. 2013, Hongois et al. 2011, N'Tsoukpoe, 2009).

Studies by others have shown that another common commercial product, silica gel, is a suitable TES material with a capacity of 0.62 MJ/kg at hydration temperatures above 100 °C (Tahat et al. 2001, Lim et al. 2017). Generally silica gel is less expensive than zeolite, also the lower dehydrating temperature compared to zeolites is interesting although slow chemical reaction kinetics may become an issue. Still, at the dehydration temperature 65 °C it is possible to obtain a TES capacity of 0.52 MJ/kg.

In this thesis featured in papers III - VI, the magnesium carbonate hydrate (MCH) from mineral carbonation possibilities for STES application is studied

leading to further process concept designs and system simulations. Specifically the study was focused on the nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) crystal structure.

It should be mentioned that TES by sorption seems to obtain better heat storage capacity compared to latent heat storage PCM material such as paraffines and the earlier mentioned polyol(erythritol)–polystyrene. The pricing of materials long term storages heat storage may become an economy challenge with zeolite price of 305 € (£280) /ton and polyol(erythritol)–polystyrene 1500 €/ton (raw materials) (Mahon et al. 2020, Annenkova 2020). Feasible implementation of TES requires cheaper materials and sorptive salts such as MgSO_4 at 71 € (£65) /ton that are shown to be chemically stable and suitable for TES are highly welcome. Converting this with CO_2 into a TES material gives an additional significant CO_2 emissions mitigation benefit.

The economics were not discussed or listed for all materials and storage types. However, a study of running costs cost and payback time would be an interesting and timely topic for a separate research and publication. Several heat storage materials are in conceptual phase and the results concerning economics vary largely (even with similar materials and processes).

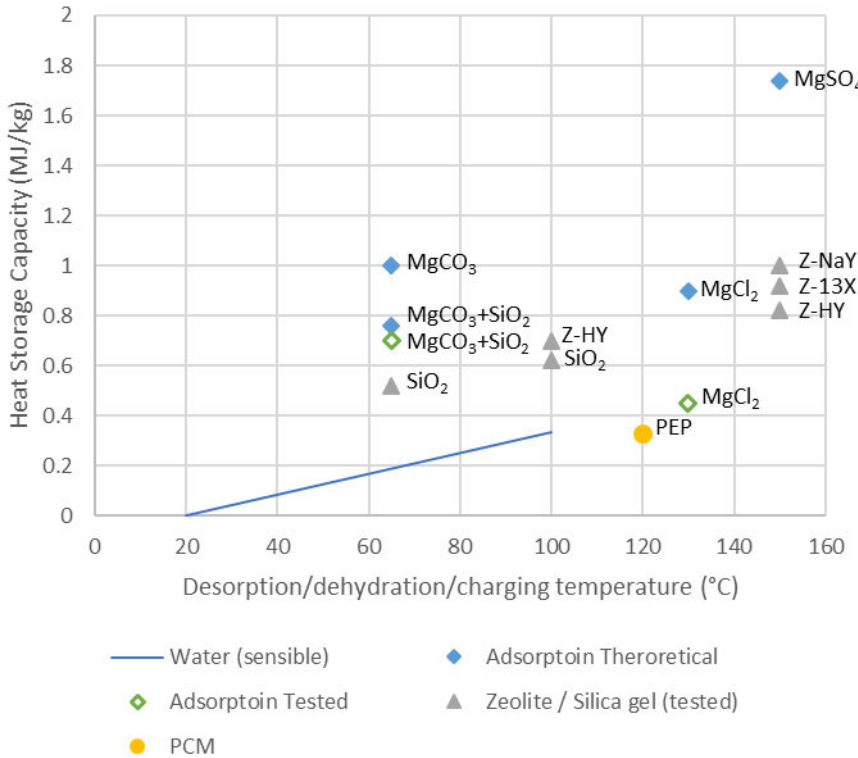


Figure 2. Heat storage capacity and desorption temperatures of a few important TES by sorption material. $MgCO_3$ (HSC 8), $MgCO_3+SiO_2$ (Paper IV-V), SiO_2 (Tahat, 2001), PEP (Puupponen et al. 2016), $MgCl$ (Zondag et al. 2013, HSC 8), Zeolites (Z) (Whitings et al. 2013) Z-HY 150°C (van Essen et al. 2008)

1.3.5. Reactor systems – TES by sorption

The basic open system TES by sorption systems in the literature are basically heat recovery ventilation systems with a sorption reactor, heating the outlet air before a heat exchanger, transferring the heat to the inlet air (see Fig 3). This is called the heat release or discharge step (Hongois et al. 2011, Zondag et al. 2013). This set up does not require high discharge temperatures to a central heating system, but simply boosts heating or pre-heating of the inlet air. In this thesis, a further developed system for the heat discharge step is presented.

The heat storing/charging step of an open reactor system is fairly simple as well. Air is heated using district heat or solar collectors desorbing the crystal water in the sorbent material (See Figure 3) (Hongois et al. 2011). As mentioned in the previous section, the desorption temperature might vary depending on the required solar collector efficiency and irradiation conditions (Paper IV).

In a closed system (see Figure 4), the heat is transferred further to a heating system (eg. space heating or hot water) using a heat exchanger (for which the design may vary). More importantly, the hydration /dehydration cycle is closed. During charging, the reactor containing the sorbent is desorbing the vapour (usually water) which is condensed and collected as a heat sink. During discharging, the heat source enables vaporisation of the liquid and transport of it to the reactor, where the sorbent absorbs/adsorbs (chemisorbs) the vapour, releasing the heat (Yu et al. 2013).

The discharging procedure resembles a heat pump, although no compressor driving power is required. Instead, the charging needed includes a solar (thermal) collector investment. It is noticeable, that the solar collector has a reasonable (depending on location) payback time also without implementing TES.

The open system's advantage is the low investment costs, considering that houses today are built with ventilations combined with heat exchangers, and solar collectors are motivated to install also without considering TES (Paper IV). Closed systems advantages are a more stable heat output (Aydin et al. 2015) and that higher output temperature with an efficient sorbent is possible.

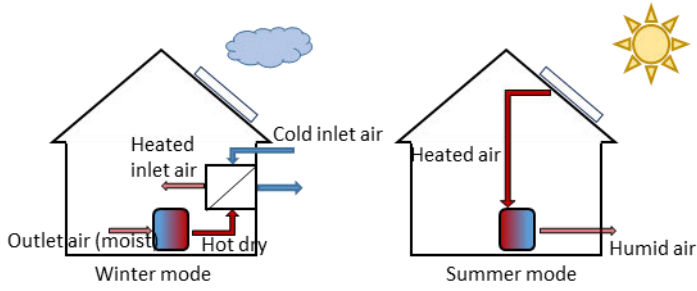


Figure 3. Open sorption system using thermal storage system by sorption. Left: heat release, Right: heat storage from solar heat (data from Hongois et. al, 2011).

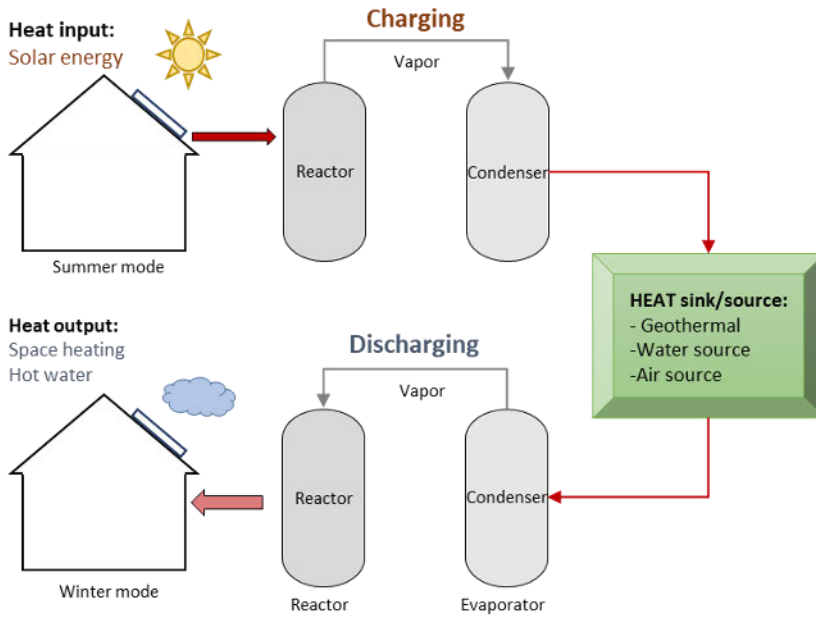


Figure 4. Closed sorption system using thermal storage system by sorption (data from Yu et al. 2013)

2. Aim of the research / research questions

The thesis is a continuation of the research of earlier work (as described above) on the CCSM process (ÅA route) developed at Åbo Akademi University. The first two papers (Papers I-II) address the possibility to find suitable rock closer to the CO₂ emitting industry. Moreover, the study compares solid/solid and aqueous/solid extraction of magnesium from the rock minerals and suggests new mixtures of extraction salts. The advantages of both methods are determined by energy (heat) requirements and are decisive for the most feasible process alternative.

Full-scale CCSM process capturing large amounts of CO₂ would produce abundant amounts of MCH, for which a purpose or application is needed to increase the motivation for a CCSM process.

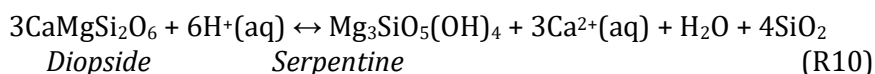
Firstly, the objective of the work reported in paper III-IV was to develop MCH product for TES. In theory, multiple times the thermal energy can be stored in MCH in form of a NQ sorption reaction compared to the same mass of heated water.

Two questions are addressed: Will it be possible to design a reactor by using MCH as a sorbent for TES? And: Where and when is it useful in practice (operating temperatures) and which process is preferable?

Secondly (Papers V-VI), after designing the sorbent material for the reactor, and its process concept, the next objective was to determine the efficiency of the process in a small pilot according to the concept and simulations based on the its data.

3. Magnesium extraction from silicate rock: materials and methods (Paper I – II).

Earlier studies had shown that serpentinite containing serpentine or lizardite mineral is suitable for solid/solid extraction (Nduagu, 2012; Romão et al., 2013). In this study, reported in papers I + II, mineral resources closer to the Turku region were tested, to decrease the energy requirements and the CO₂-penalty due to transport. The earlier tested and suitable serpentinite (Serp-A) resources is located 500 km from a CO₂ producer near Turku. Two other rocks were located 100 km from Turku, which are Mg-hornblende and another serpentinite (Serp-B) mine tailing. A third rock, a Mg-rich diopside was found at the limestone quarry next to a lime kiln at Parainen. Shown in Table 1, the magnesium amount in the serpentines is considerably larger. Studies by others suggested that serpentine can be produced from diopside (see reaction R10) in acidic aqueous solution (Lu et al., 2011) – unfortunately this could not be reproduced in the laboratory!



Interestingly, other authors (Sanna et al., 2014) have reported that pyroxenes are chemically very stable in an acidic environment. Pyroxene minerals containing diopside leached in an aqueous ammonium bisulphate (ABS, NH₄HSO₄) showed that 30% of the magnesium was extracted at 3 hours. The less stable olivine (Norway) showed a Mg-extraction of 70% and from lizardite-type serpentinite (Scotland) more than 85 % could be extracted within 3 h. (Sanna et al. 2014, Styles et al., 2014).

3. MAGNESIUM EXTRACION

Table 1. Chemical compositions of the minerals tested, based on XRF analysis. Ign.l. stand for ignition loss. (Analyses from Nordkalk Oy Ab, Parainen, Finland). Elements with mass below 1%-wt are not shown. Unit: dry %wt.

Compound	Serp-A	Serp-B	Diopside	Mg-Horn
CaO	0.4	0.45	23.8	10.9
SiO ₂	35.5	35.3	49.9	48.7
TiO ₂	0.04	0.15	1.2	0.85
Al ₂ O ₃	0.45	2.7	2.9	14.7
Fe ₂ O ₃	14.6	16.3	14.2	12.1
MgO	35.1	31.0	6.6	8.7

3.1 Solid/solid and aqueous/solid extraction

In the solid/solid extraction, described in section 1.2, the grinded mineral (typically around 0.1 mm) and the solvent salt ammonium sulphate (AS) and/or ammonium bisulphate ABS (optionally with small amounts of added water) react during typically 30 minutes at typically 440 °C. For the experiments, a rotary tube/kiln and a chamber furnace were used. For the tests ceramic crucible containers and in the rotary tube, a quartz glass tube was used. After the extraction the sample is cooled and dissolved in distilled water and the unreacted and insoluble products part of the minerals from the rock is filtered off. The solid/solid extraction method for producing MgSO₄ reaction intermediate from magnesium silicate- based rock was developed in earlier research at Åbo Akademi University (see e.g. Romão dr thesis 2015, Nduagu dr thesis 2012).

The aqueous/solid extraction follows a more simple procedure. The chosen fraction of grinded mineral is stirred in a 1.4M AS and/or ABS aqueous solution for a certain time (eg. 2-3 hours). Again, the unreacted and insoluble material is filtered off, and the Mg-rich solution can be used for further carbonation in the ÅA-route process (Option 1 and 2 for gas/solid and Option 3 for gas/aqueous carbonation).

More details of the methods solid/solid and aqueous/solid extraction methods can be found in Papers I and II, respectively. The key findings of the study is discussed in section 6.1.

4. Material properties and development

The seasonal TES (STES) material was developed and improved in several stages (Paper III, IV, V). Chapter 4 describes TES material development and its complex properties, involving quite a few stages leading to new test series based on earlier results. The sorption and durability properties are also described in this chapter.

4.1 Magnesium carbonate hydrate (MCH)

The most discussed configurations of magnesium carbonate hydrate (MCH) are nesqueonite (NQ), hydromagnesite (HM) and dypingite (DG). As mentioned in section 1.2 nesqueonite has a higher (1:1) carbonate per magnesium ion (CO_3/Mg) ratio than hydromagnesite and dypingite (4:5). The higher CO_3/Mg -ratio makes the NQ more desirable as a CCSM product. According to Hill et al. NQ degrades rapidly to HM or DG (discussed in section 4.3.1) at higher temperatures, and over time at room temperature (discussed in section 4.2.3) (Hill et al. 1979). This makes extensive studies on NQs stability necessary. Moreover, for this study, it is of main interest to determine under which conditions NQ is stable. HM and DG are not suitable for TES, as the dehydration reactions are hardly reversible and the amount of crystal water per mass is very low.

4.2 Hydration –initial tests of MCH

Initial test revealed that magnesite (MgCO_3) as such is not a reactive desiccant as other typical minerals tested by others for the purpose (such as MgSO_4 , CaCl_2 or KCl). MgCO_3 powder in a humid atmosphere was found able to absorb water vapour resulting in a roughly 5% mass increase, although according to reaction (R8), theoretically the stoichiometric mass increase would be 64%.

Stirring the powder a few times during the process increases the mass increase to 9-12%, which is still not sufficient for a TES application. Another approach, producing NQ ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) as granules and filter cakes and dehydrating the material, resulted in just a few percent mass increase during re-hydration. The improved adsorption and/or water absorption when stirring the powder and the decreased mass increase resulted in longer transport distances for the gas to granules and cakes, which indicates that the contacting of the gas and the material (i.e. heat/mass transfer) needs to be improved. Moreover, it is not necessarily a crust layer (of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) that needs to be avoided as mentioned earlier in the case of MgSO_4 (Hongois et al. 2011). The objective for

this test series was to understand under which conditions the material adsorbs water and how much.

4.2.1. MCH - silica gel mixtures (Paper III)

Early tests on the actual absorbance capacity of the MgCO_3 were done with pre-wetted silica gel (SG) mixed with MgCO_3 as magnesite and dehydrated NQ (DNQ) in a humid atmosphere. Silica gel would channel the water molecules to the MgCO_3 and allowing absorption of more water from the surroundings. The DNQ sample showed a mass increase of 100% (partly absorbing water as liquid) while the magnesite sample was able to absorb to a less than 15% mass increase. Simple filter cakes with a mixture of 50% silica gel and 50% DNQ for 48 hours in a humid atmosphere gave a mass increase of 24%, corresponding to 36.5% conversion according to reaction R8 and giving a calculated TES capacity of 0.37 MJ/kg.

Testing the hydration capacity by measuring the mass increase is a common method to determine and record the effect over time, especially for silica gel (Tahat, 2001). At this point however, measuring the small samples' heat effects was not possible, but this was done later in the research with larger samples. The smaller samples enabled testing more samples at once, though.

4.2.2. Production of nesquehonite (NQ) and preparations of composite material

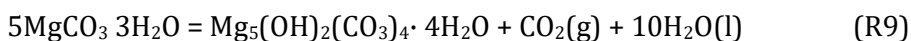
Laboratory quality MgSO_4 (purity 99.5 %) was dissolved in water (instead of silicate minerals as magnesium source according to the ÅA-routes) was used for producing NQ for TES tests to secure consistent results for TES material tests. The solution pH was increased with ammonia (according to the ÅA-routes) to around 9.5 and temperature kept below 30 °C (note: exothermic reaction) in order to precipitate NQ according to reaction (R7). Scanning electron microscopy (SEM) tests showed that the product was indeed pure NQ. Interestingly, no sulphur was found using EDAX element analysis after one or two times water rinsing the NQ filter cakes.

Noticeable is that NQ is very porous when filtrated after precipitation, however re-dissolving it in water and re-filtering the material (or dry it) decreases the volume significantly. This needs to be considered when producing the mixture of NQ and silica gel (eg. if mixing the two components in the filter cakes after first filtration). For production of the granules, the silica gel was saturated with water and the NQ was dissolved in a small amount of water. The amount of water was adjusted for the mixture to form a mouldable paste. The mixture was dried (desorbing water) in a 20% CO_2 and 80% air (vol/vol) atmosphere. Various silica gels (particle and pore size) were used at different

stages of the study. The same method was used later when plates on a plastic grid support were produced instead of granules.

4.2.3 Sorption in a closed system TES Concept (Paper IV)

To prevent NQ from emitting CO₂ and degrade to HM or DG, the first idea was to use a closed system TES. Dehydration tests showed that at temperatures around 50 – 65 °C the dehydration (storing energy/heat by releasing crystallization water) of NQ, forms DNQ according to reaction R8. To prevent degradation of NQ (see reaction R9), the CO₂ concentration has to be higher than that in the atmosphere according to several studies. (Hill et al. 1979, Jauffret et al. 2015)



For discharging energy/heat in the hydration step, temperatures of 5 – 25 °C were shown to be suitable. The closed system uses geothermal heat to evaporate water increasing the RH and the TES reactor absorbing water vapour results in a heat generator, as established in earlier studies by others (Yu et. al. 2013). A more detailed description of the closed system concept for NQ and methods can be found in Paper IV.

To determine the performance of the NQ + SG mixture in a simple closed heat storage system, the hydration capacity at various relative humidities (RH) was tested. Shown in Figure 5, the mass increase of 0.2 g/g_{sample} (sample 1) can be reached at 40% RH (calculated heat effect 0.32 MJ/kg). A RH of 75% would give a mass increase of 0.25-0.29 g/g_{sample} and for another sample (2) with very small particle size (500-1000 nm) on the silica gel a 0.41 g/g_{sample} mass increase was found (calculated heat effect 0.68 MJ/kg).

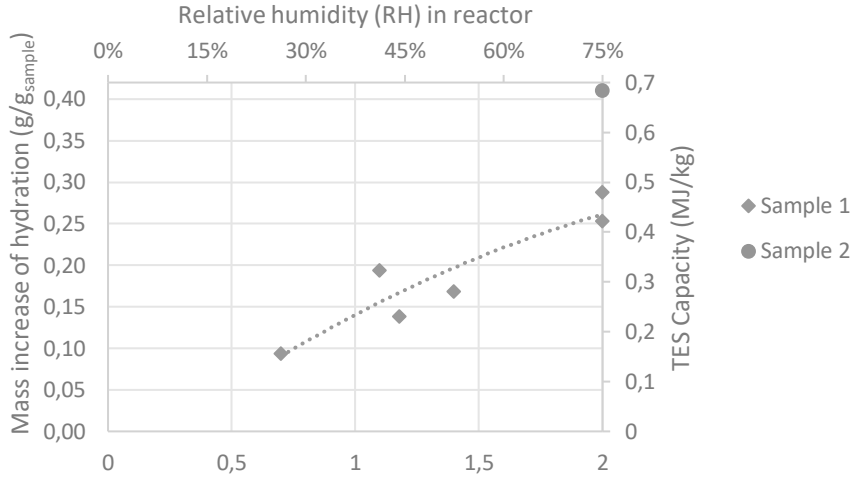


Figure 5. Mass increase of hydration and TES capacity versus relative humidity (RH) and evaporator pressure for 50 %-wt/50 %-wt silica gel and dehydrated NQ, and pure silica gel for reference (Experiment duration 48 h). (Paper IV)

4.3 Dehydration

A Gibbs energy minimization simulation using HSC Gibbs free energy minimisation software shows that NQ will be formed at lower temperatures, in other words, almost full desorption will appear at 20 °C. Magnesite or DNQ will be formed as 0.5 moles each above 45°C while 0.9 moles of magnesite with 0.1 moles DNQ will be formed at 61 °C.

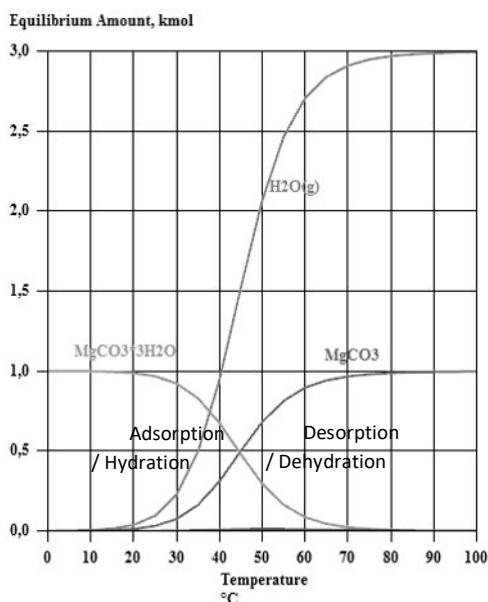


Figure 6. Gibbs energy minimization with $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ as reactant (1 mole). The calculation follows to reaction R8 (Paper III).

The theoretical conversion calculated using Gibbs free energy minimization (see Figure 6) is comparable with findings from the dehydration tests of NQ after 120 minutes (stable). Already at 50 and 55 °C a desorption of 90% and 92% was obtained, respectively. Similar results were obtained in studies by others for an open system, although no conversion was reported for a closed and wet/humid system (Morgan et al. 2015).

At a temperature of 65 °C, full desorption was reached, giving also the target temperature for this work for the dehydration process. Silica gel, the other component of the composite material, requires around 100°C for full dehydration (0.62 MJ/kg). A test showed that dehydration at 65°C will still be able to store 0.52 MJ/kg of heat, being still sufficient. Increasing the dehydration temperature closer to 100°C could result in more HM production (with loss of CO_2) after several cycles but also misses the advantage of low dehydration temperature.

The NQ+SG samples of only a few grams were dehydrated with an overflow of heated air until the mass stabilized (after around 2 hours). The larger samples (more than 50 g) were dehydrated in the testing reactor (with hot air, inlet around 70 °C) until the outlet air specific humidity (SH) and RH matched the inlet air.

The overall results of these hydration and dehydration test methods are discussed in the key findings, in section 6.2.

4.4 Material analysis – aging, cycling

Materials used for TES need to be durable and stable and remain their properties despite of several cycles of reaction. The earlier mentioned risk of NQ degrading and emitting CO₂ according to (R9) was examined under actual TES conditions. The material performance of chemisorbing water vapour did not decrease during more than twenty cycles (dehydrate and re-hydrate), using a granulated samples with (D)NQ and SG. In fact, the mass increase (hydration performance) slightly improved during the first cycles. On that particular sample, only small amounts of HM were found, less than 1-wt%.

According to Hill et al., NQ forms HM at 25 °C in an atmosphere with < 1% of CO₂, and at 10°C below 0.1% of CO₂. The rate for this reaction is unknown and the equilibrium is untested (Hill et al. 1979).

The risk of HM formation according to reaction (R9) (emitting 1 out of 5 CO₂ from NQ, not reversible) during the hydration process was tested and monitored by scanning electron microscopy (SEM) (Jauffret et al. 2015). The shape of NQ can be seen as needle shaped crystals (e.g., Figure 7a) and HM can be seen as irregular flakes (e.g. partly in Figure 7b) (Morrison et al. 2015, Teir et al. 2007). Samples stored under atmospheric conditions were compared to samples kept in a CO₂ rich atmosphere. Very small changes were visible after one 1 and 2 weeks and after 2 months the sharp needle shaped NQ slightly rounded ends, however, no HM was visible.

As already mentioned above, according to Glasser et al. (2016), compressed NQ becomes a more or less agglomerated or ill-crystalized phase called “phase X” (Glasser et al. 2016, Jauffret et al. 2015). Shown in Figure 7a and 7b, the NQ has been dehydrated and re-hydrated, and the so-called “phase X” is visible. It can be summarised that most of the mass after one (Figure 7b and Figure 7a) or twenty cycles is a magnesium carbonate hydrate (MCH) called “phase X”, besides very small amounts are HM, and crystalline needle-like NQ. More importantly, this configuration of MCH, ill-crystalline NQ (or “phase X”), is still able to chemisorb

and desorb water vapour sufficiently for a TES system (up to 0.72 MJ/kg mixed with silica gel).

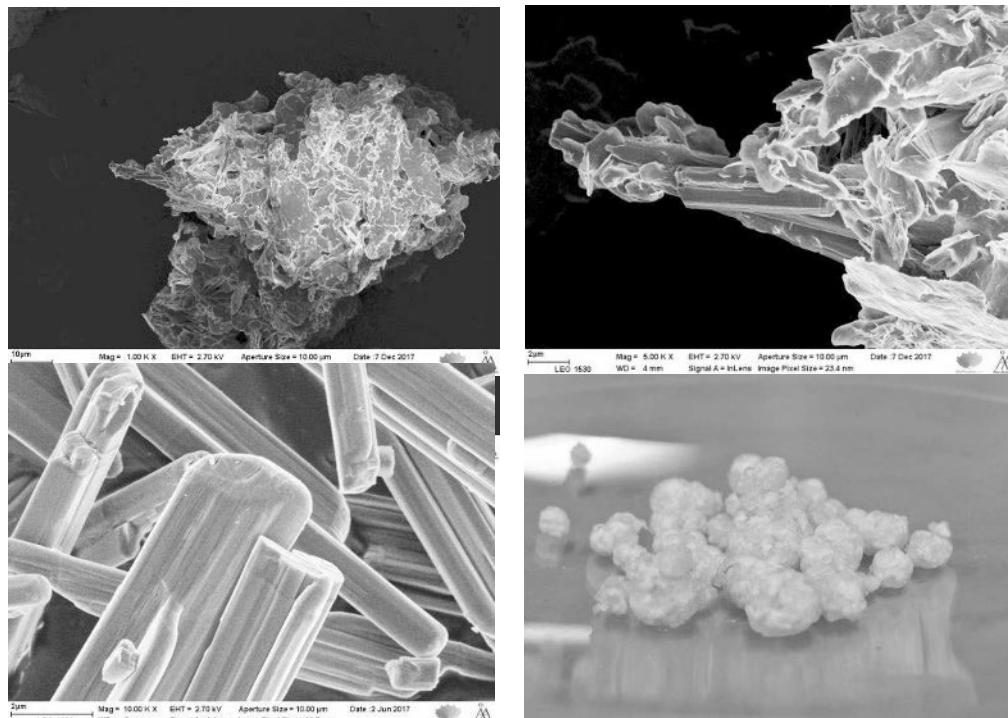


Figure 7. SEM pictures of sample used in at least 20 cycles of reaction R8: **(a)** 1000 \times and **(b)** 5000 \times , **(c)** Unprocessed nesquehonite in room temperature at atmospheric CO_2 -pressure for 2 months. **(d)** Picture of NQ+silica gel granules tested (NQ is white, the yellow colour is from the silica gel product).

4.4.1. Thermogravimetric analysis

In section 4.3, the dehydration reaction is primarily tested to find a suitable temperature range for maximum chemical conversion according to reaction (R8). The degradation of NQ resulting in HM at too high temperatures should be carefully considered during dehydration, to minimise the aging with time at (too) high temperatures and many cycles.

The desorption enthalpy for the silica gel has been experimentally determined in studies by others, even for TES purposes (Tahat, 2001). Experimental data confirming thermodynamic data for dehydration of NQ that would support the calculations with HSC (version 8) have not been found in the literature. Thermogravimetric analysis (TGA) measurements were therefore done to determine the enthalpy of the heat effects of a mixture of SG and NQ..

The method measures both heat effect (as temperature difference with a reference material) and mass change (decrease) in order to determine the enthalpy. In Figure 8, specific heat is calculated from both mass decrease (dm-data) using reaction enthalpy and temperature difference (dT-data) using the specific heat capacity determined using dm-data, depending on the temperature of the samples.

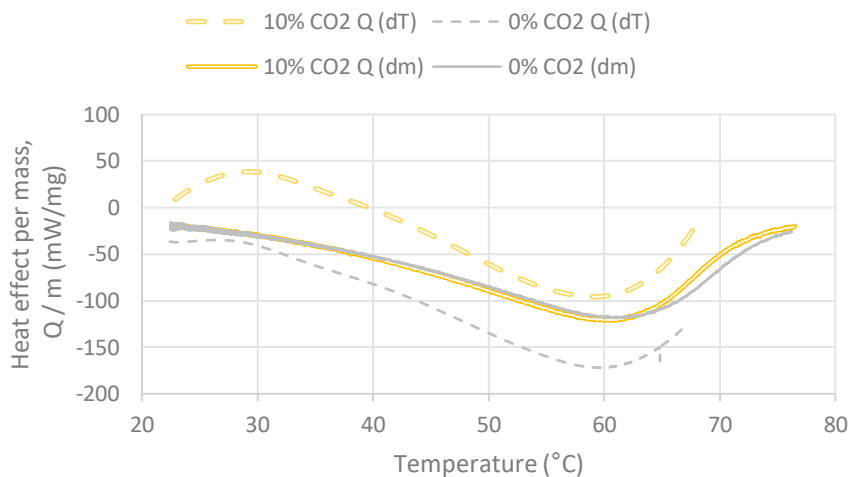


Figure 8. The dashed lines show the values calculated from temperature difference data using specific heat values for the materials. The dotted line shows the value calculated from mass difference data using the reaction enthalpy. First test (yellow/double line) had 90% N_2 and 10% CO_2 as reaction gas, and the second test (grey/single line) had N_2 as reaction gas.

Dehydration of the testing materials typically implied dehydration in an atmosphere containing at least 10% CO_2 mixed with air to maximize the number of cycles of NQ, without degradation to HM. Therefore, tests reported here were done with both 10% CO_2 (yellow line) and 90% nitrogen gas with the other test in 100% nitrogen (grey line).

The specific heat from both dm-data and dT-data should match, if the enthalpy and specific heat capacity figures obtained with the materials are correct. The sample tested in the TGA in 10% CO_2 shows only small visible differences between the values for the operating temperature range of the dehydration (50 - 65 °C).

The sample produced in a nitrogen gas atmosphere shows a larger difference, which could imply heat effects from the material emitting CO_2 . However, the gravimetric data shows a heat effect at higher temperatures while the temperature data ranges stops at a lower temperature. Considering the

relatively quick temperature increase of 4 °C/min used during the tests, the differences between the two results might be caused by a delay.

Around 60 °C the specific heat found is the highest for both tests and the dehydration kinetics are fastest. The reaction has reached a higher conversion already at 60 °C compared to the conversion at 45-55 °C (part of the dehydration takes place at 40-55 °C). This may decrease the reaction rate (visible at 60 °C) shown in the TGA measurement compared to unconverted (eg. typical start of dehydration) NQ at 60 °C. This suggests that the correct maximum kinetic value (in the TGA measurement) is actually found at a slightly lower temperature.

5. Process systems and simulations

5.1 STES Open reactor systems and relative humidity (RH)

The tests showing that no NQ degradation (resulting in HM of DG) of the material occurs during hydration under the conditions tested enables chemisorption in open system TES reactors using NQ.

Several open system TES concepts suggested in the literature involve heating of house outlet or exhaust air by reacting with a sorption material during the heat discharge phase (Hongois et al. 2011, N'Tsoukpoe et al. 2009). In a relative simple set up, the heated and dried air (outlet) can heat up the house inlet air using a heat exchanger.

During the heating period (while obtaining heat from the TES system), the outside temperature is typically from 10 to -20 °C, which results in low relative humidity (RH) at room temperatures. The maximum indoor RH of inlet air is 25% (at 21 °C) when the outdoor temperature is 0 °C, resulting in an outlet RH around 30 - 40%, due to several indoor activities (shower, cooking etc.) and plants. The indoor RH is somewhat lower when outdoor temperature decreases. These levels of relative humidity (RH) more or less compromise the storage capacity, regarding the most common TES by sorption materials (such as silica gel, MgSO_4 , MgCO_3) (Lim et al. 2017). Shown in Figure 5, at least 40% indoor RH is required for sufficient and useful results with NQ, preferably 70%.

5.2. The concept - Open reactor coupled with an exhaust air heat pump (EAHP)

In certain TES closed systems, external heat sources for evaporation can be used to increase the RH, which might be complicated and expensive. Another measure to increase the RH in an open system TES reactor is to decrease the temperature. For this, it is possible to combine an open system TES reactor with an exhaust air heat pump (EAHP). A standard EAHP decreases the temperature of the exhaust indoor air (containing water vapour) of a building, cooling that air to eg. 4 °C and collecting the heat (for a water based heating system). The exhaust air RH is then increased to 60–100% and this becomes the inlet air for the TES reactor, if connected according to the concept shown in Figure 9.

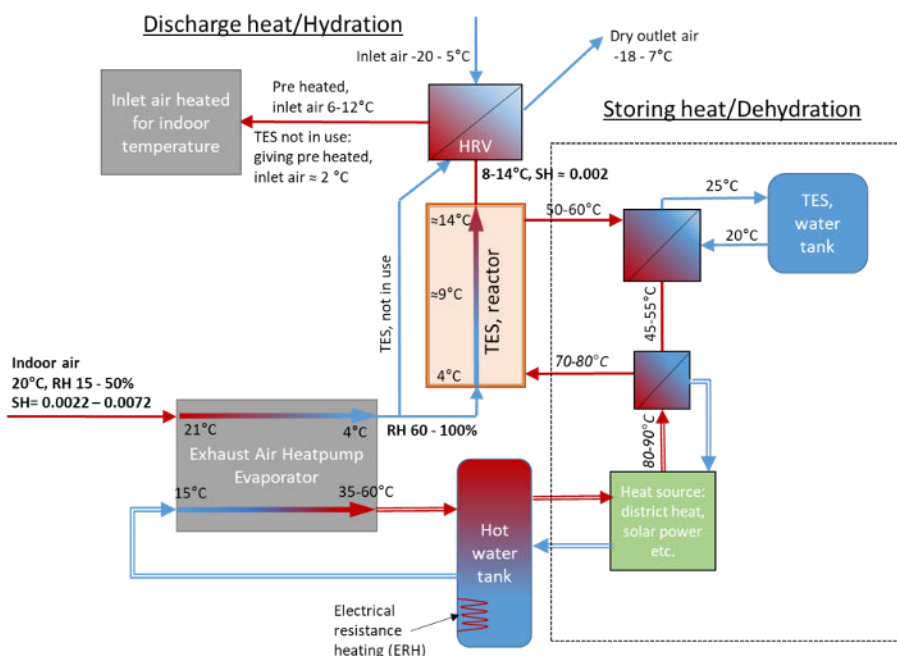


Figure 9. Process scheme of the concept, presented in earlier work (Paper IV, V and VI). Thermal energy storage reactor combined with an exhaust air heat pump system. Simple line arrows contains gas/air flow, double lined contains liquid.

The RH, SH, temperature and enthalpy for every stage for the air, following the concept, are illustrated in Figure 10 and 11. The air temperature rises by 5-8 °C in the reactor. In a standard EAHP system, the 4 °C air goes to a heat exchanger, providing the rest of the heat to the house inlet air (if the outdoor air is below 4 °C). The TES reactor can simply be installed between the EAHP and the heat exchanger (see Figure 9). This set up results in a larger heat storage capacity for a reactor using the NQ and silica gel composite.

In the case of minimal ventilation (Finnish regulations), a 100m² and 250m³ house, would have ventilation flow of 125m³/h. The heat output varies depending on the RH of the outlet/exhaust air however, at 100% RH the heat output would be around 1.5 kW. The heat exchangers in exhaust air heat recovery systems are usually up to 90% efficient, depending on the design and size (O'Connor et al. 2016). In this concept 85% effectivity is used, to minimize the loss of heat generated by the reactor.

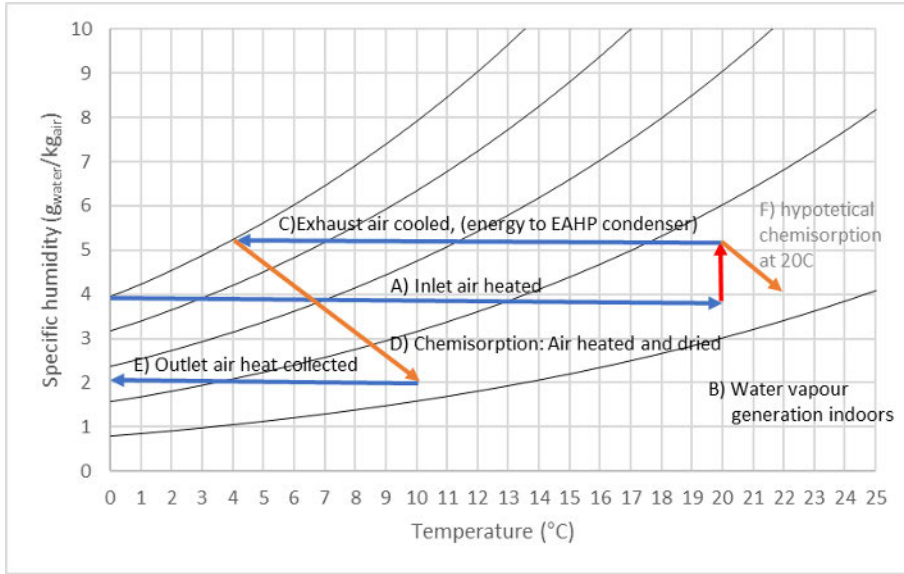


Figure 10. The temperature and SH of the process steps. A) the inlet air reaches the indoor temperature, B) water vapour generation of human activities increases the RH and SH. C) the outlet/exhaust air temperature decreases in the heat exchanger connected to the EAHP condenser. D) The temperature increases and SH decreases as a result of chemisorption. E) the heat is collected (heat to inlet air) in the heat recovery ventilation system, and the temperature decreases to near outdoor temperature. F) Chemisorption without EHAP, heat effect only a fraction compared with D (for comparison).

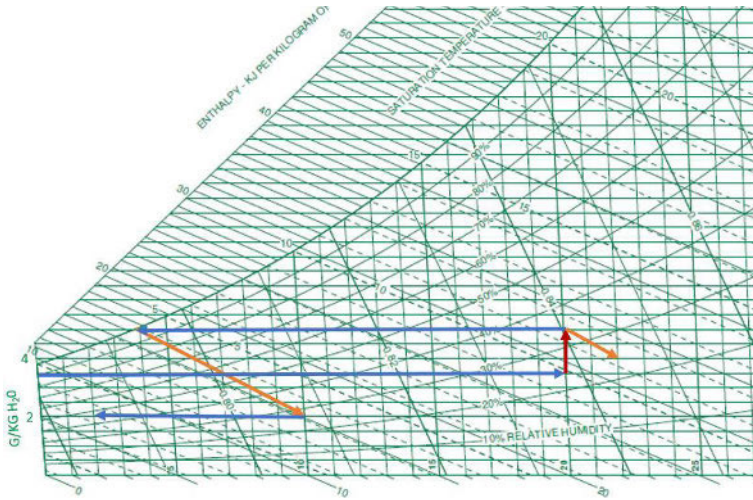


Figure 11. The similar example shown in Figure 10 is illustrated in a psychrometric chart cut out (pharmaceuticalhvac.com)

An EAHP alone is usually not sufficient and requires an auxiliary power or heat source for colder days (Fracastoro, et al. 2010). However, often an electrical resistance heater is used as auxiliary heat source, which steepens the peaks of electricity demand a cold day. The numbers of annually installed EAHP systems has been rising during the last two decades (Motiva 2020). Adding a heat source that is not using electricity to every EAHP would decrease the use of emergency power plants (usually burning fossil fuels) during winter time.

Experimental studies by others show that a modern typical and/or popular EAHP gives a COP around 3.4 while producing 35 °C heated water (for floor heating), and 3.0 when 55 °C heat is produced (Mikola and Kõiv, 2014). Obviously, combining EAHP and electrical resistance heating decreases the COP and the smaller part of the required heat the EAHP can provide, the lower the COP value will be. Shown in Figure 12, the COP increases by integration with STES during colder periods. The calculations of the results in Figure 12 are based on a modern 100 m² attached house, located in Helsinki, Finland assuming 100% RH outdoors. In this example, the house air volume is 250m³ and the ventilation air flow 125m³/h and the outdoor RH 100% at every temperature. Winter-time when the TES reactor would be in use, the RH is most of the time close to 100%.

The outdoors temperatures is a large part of the year (3000 - 4000 hours) between -10°C and 0 °C in a Nordic coastal climate, which is the temperature range where the STES boosts the COP most, resulting in an improved energy efficiency. This concept would simply make EAHP a more attractive choice, with the right pricing.

A more detailed simulation was made for this system concept, and is explained with results presented in Paper VI. The simulation was done for a whole year (July 2018-June 2019) heating using temperature and solar radiation data from weather station (REF) for a house in Helsinki.

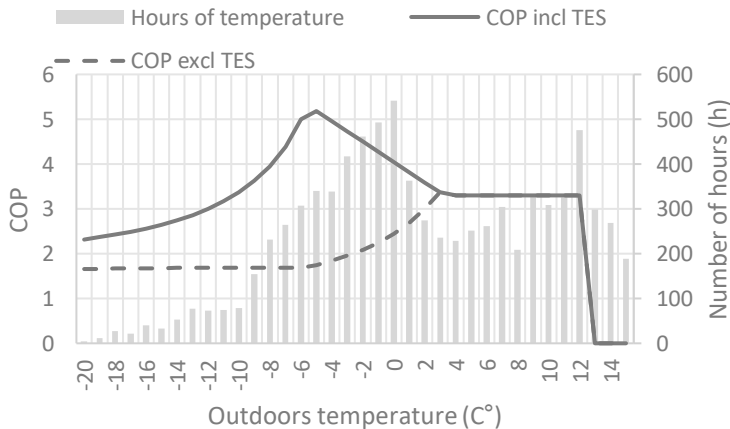


Figure 12. *The coefficient of performance (COP) with and without the thermal energy storage (TES) reactor, and the number of hours for varying outdoor temperature (Paper VI).*

5.3. Set-up for concept testing (kinetics and enthalpy) (Paper V)

The heat effect of completely (re-)hydrating the dehydrated/desorbed samples (according to reaction R8) was measured using thermocouples (type K, ± 0.1 °C at 25 °C) and humidity measurement (DHT22, ± 2 % RH at 0–100% RH collecting data every 30 seconds (pico logger), giving the necessary data for the kinetics depending on the conversion and for determining the enthalpy of the chemisorption reaction. The flow for the peristaltic pumps used were measured several times, and the flow seemed to be very stable. The heat effects and conversion kinetics are calculated based on temperature increase, which has been the obvious method in studies by others (Hongois, et al. 2011, Zondag et al. 2013).

Shown in Figure 13 is the set-up for testing the kinetics of laboratory system simulating the concept described above. A picture of the set up implementation and the test reactor are shown in Figure 14. For the inlet of the reactor air a required specific humidity was produced by mixing 100% relative humidity (RH) air produced at room temperature and completely dried air. For obtaining $\sim 95\%$ RH in the reactor inlet the air is dried in a condensate collector to ensure that no liquid water is pumped into the system, compromising the results by not adding any heat while adding mass. The system where the enthalpy was measured was insulated and its conductivity was determined.

For these experiments 2 mm thick plates with integrated plastic support were used, to overcome the challenges with strength of the composite material when producing granules. Another measure to add strength was smaller ($150\text{--}250\text{ }\mu\text{m}$) particles of silica gel (earlier $0.5\text{--}1\text{ mm}$) and additionally improving the homogeneity of the NQ + silica gel material mix in the reactor. The sample size used in the reactor was 70 g. The overall results and key findings are discussed in section 5 can be found in section 6.2.

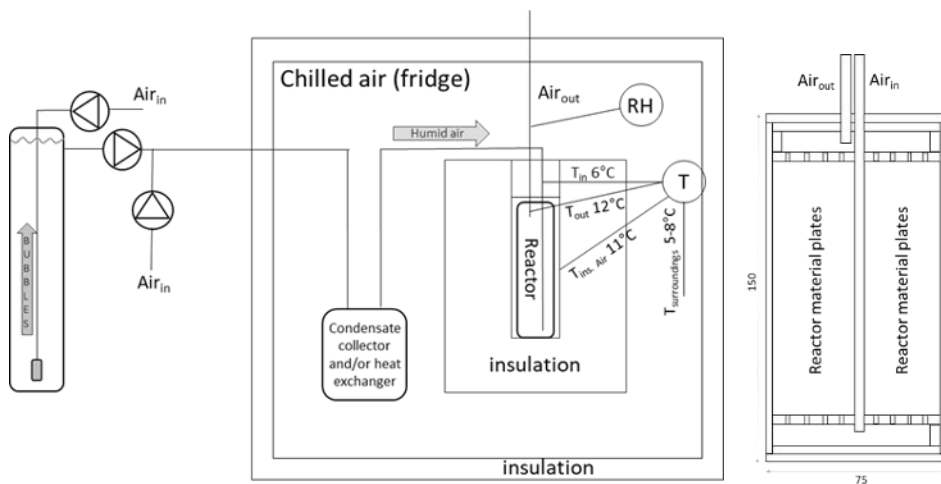


Figure 13. (a) (left): Scheme of the experimental set up and typical temperatures around the insulated reactor. Inlet air RH is generated by mixing water vapour saturated air (from the bubble column) and dry air. The chilled air around the reactor insulation simulates the outlet temperature of the EAHP including a condensate collector eliminates liquid water in the reactor. Temperature is measured at the reactor air inlet and outlet. For heat loss analysis, temperatures of the air between the reactor and insulations and the surroundings are measured. RH is measure of both inlet and out let air. **(b)** (right): Scheme of the reactor. Reactor material plates with mixed NQ and silica gel are mounted vertically.



Figure 14. (a) Top: picture of the set up according to the scheme in Figure 13 (excluding the water vapour generation), (b) Bottom right: reactor vessel seen from the outside (c) Bottom left: inside the reactor.

6. Key Findings

6.1. Extraction (Paper I – II)

The alternative (for serpentinite) magnesium source minerals, Mg-Hornblende and diopside were insufficiently effective for extracting magnesium. In tests with aqueous/solid extraction, only a few percent of the magnesium in the material was extracted. Test with solid/solid extraction resulted in almost no extraction at all. These two minerals would require more mineral per fixed CO₂ (see Figure 15) to begin with, considering that both contained less Mg than the other ones. The extraction of calcium from diopside was insufficient as well, thus aiming at CaCO₃ product instead is not feasible either. Mentioned in section 3, according to Lu et al. 2011, diopside would form serpentine after calcium extraction (see reaction R11) which could however not be verified.

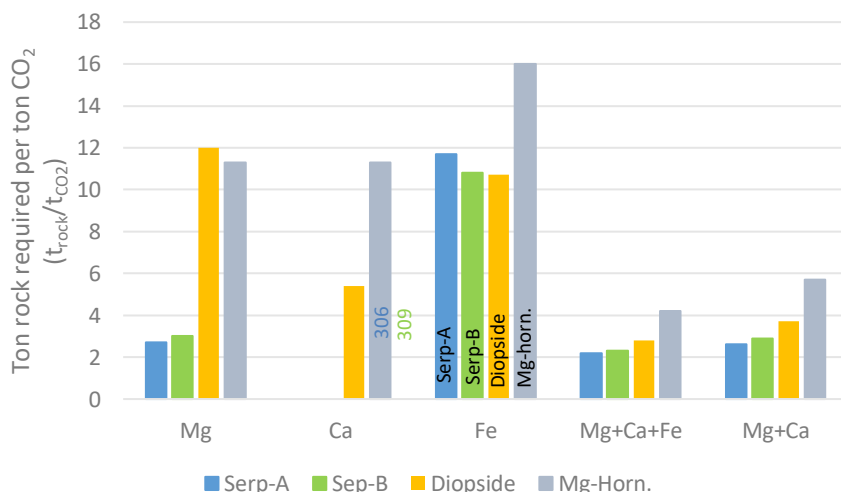


Figure 15. The Mg extraction from serpentinite is dependent on pH and particle size. Binding capacity of the best Finnish serpentinite is 292 kg CO₂/ton rock (Paper I data).

The magnesium extraction from serpentinites is on the other hand sufficient with both extraction methods, as stated in earlier studies by others (Nduagu et al. 2012, Styles et al. 2014). Magnesium extraction up to 75-80% was in this work obtained in 0.7 M ABS + 0.7 M AS in water. The earlier known tested Serp-A reaches the final result faster than Serp-B. The thermal solid/solid gave a magnesium extraction of 60-65% from the serpentinites. The reactivity is clearly better and it will save energy (and/or reaction time) when partly substituting

the acidic salt ABS with AS. Serp-A seems to be the more suitable when compared to Serp-B.

Figure 15 shows the stoichiometric amount of mineral material (tons) required per ton CO₂ stored.

The recycling or re-generation of ABS acidity mentioned in section 1.1.2, should be simplified, considering the considerable investments and/or energy input requirements. This motivated testing of (partly) substituting ABS with AS in various ratios, of which the results are shown in Figure 16. Noticeable is that substitution half of the ABS with AS obtains efficient extraction, although the reaction rate reaching the same extraction is compromised compared to using ABS alone. The results in Figure 16 give valuable information for dimensioning and minimizing the energy use (and/or reactor volumes due to shorter residence time) if ÅA-route option 3 is chosen.

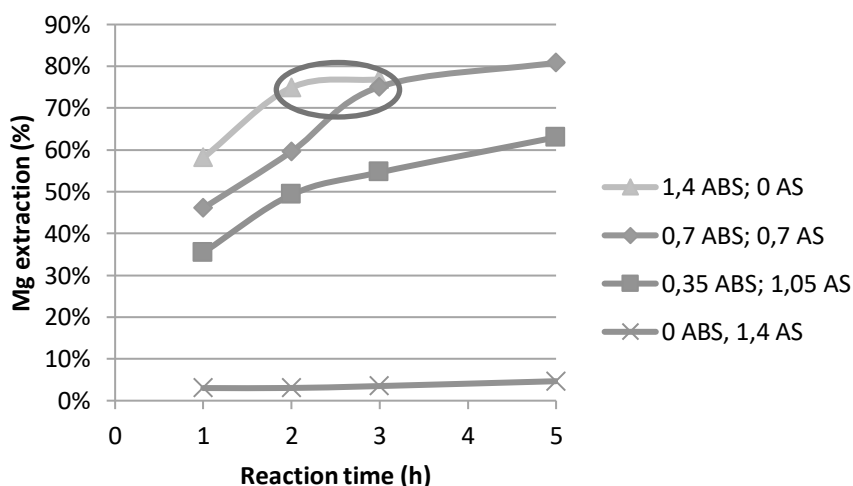


Figure 16. Extraction of magnesium from Serp-A in 0.4 l 1.4 M ammonium salt with various amounts of AS substituted with ABS. (Paper II)

In Table 2, the main differences between aqueous/solid is solid/solid extraction are listed and compared. The choice between these two extractions may depend on waste heat types and temperatures available at the CO₂ producer or the nearby industry. The CCSM process does not necessarily require to be located next to the CO₂-emitting unit. However, available waste heat decreases the (external) heat and power consumption of the process.

6. KEY FINDINGS

Table 2. *A comparison of the specifications and the results between thermal solid/solid and aqueous liquid/solid leaching. (Paper II).*

Extraction method	Solid/Solid	Solid/Liquid Leaching
Sublimation of NH_3	High temperature (440 °C) required in the reactor.	Generation of ABS out of AS at 330 °C or other re-generation method (see route 3b in section 1.2). Only half of the AS has to be heated.
Heating of water masses	Absence of water in the reactor. Less energy used for heating (440 °C)	Water and the reactants are heated to the reaction temperature of 70 °C–90 °C
Reactivity and kinetics	Reaction time 60 min, typically 60-65 % Mg-extraction of Serpentinite.	Reaction time 120-180 min, typically 75 % Mg-extraction of Serpentinite.
Total use of water in the process	Water needs to dissolve the produced MgSO_4 , which is highly soluble	For 25–50 g rock, 1 l of water is used
External/Waste Energy	High temperature external heat is needed (extraction temp. 440 °C)	Less high temperature external heat (330 °C) is needed, only a part of the AS forms ABS. Low temperature external heat needed (extraction temp. 70 °C–90 °C)
Use of solvent	1.15 to 1.5 stoichiometry of solvent salt is needed compare to the extracted elements of serpentine	A molar ratio > 3 of solvent salt compared to the extracted elements of serpentine. (only half generated)

6.2 Hydration / Chemisorption results (Paper III, IV, V).

The hydration (heat storage) capacity of a few grams granule samples increased while the composite material containing NQ and silica gel was developed, which is discussed in sections 4.1 and 4.2. Another measure that improved the TES system test results was assuring that the reactor outlet air during the dehydration was dry, in addition to monitoring the weight and time.

The best result at 25 °C was a mass increase of 0.41 $\Delta g/g_{\text{sample}}$ and a calculated 0.68 MJ/kg heat storage capacity with a silica gel particle size of 500-1000 μm . As mentioned earlier (section 5.2) the size of the silica gel particles was decreased to 150-250 μm (giving the risk that this decreases the water transport in the composite material) as to increase the stability of the composite material plates for the laboratory pilot reactor. By using that silica gel particle size in the mixture granules, the mass increase was 0.46 $\Delta g/g_{\text{sample}}$ and the calculated heat storage capacity 0.72 MJ/kg (see Figure 17), which is very close to the maximum theoretical value for 50%/50% mass DNQ + silica gel composite material. At 8 - 11°C (slightly higher than the 4°C inlet temperature taken for the TES system concept to simulate for the temperature increase in a reactor) hydration mass increases of 0.21 $\Delta g/g_{\text{sample}}$ and 0.37 MJ/kg heat storage capacity were obtained.

The heat storage capacity of samples with 50%/50% mass DNQ and silica gel of around 70g shaped as plates in the flow direction in was tested in the pilot reactor. The heat rate and kinetics was tested as well, and the methods were described in section 5.2. Shown in Figure 17, at room temperature, a heat effect (heat release, TES capacity) of 0.41 MJ/kg was obtained. The hydration mass increase was 0.26 $\Delta g/g_{\text{sample}}$. More importantly, an around 5°C inlet air temperature gave a heat effect of 0.29 MJ/kg. These tests were used in the simulations however, still leaving room for improvement of heat storage, as the 70 g sample achieved 63% hydration compared to the earlier 3 g sample, per unit mass. It seems that there is a mass and/or heat transfer challenge that needs more work. Also, these values are still roughly a third of the results zeolite (Whitings et al. 2013, Hongois et al. 2011). Although, the homogenous structure of zeolite (and silica gel) provides very consistent results regardless of its granular size.

Studies by others indicated similar effects with water vapour adsorption in granular minerals, and in MgCl_2 in this case, obtaining around 50% heat storage capacity in the laboratory compared to theory (Zondag et al. 2013).

Shown in Figure 17, the tests with around 5-6 g/kg specific humidity (SH) resulted in a 0.29 MJ/kg heat effect at 6-7 °C and 90-95% RH, while at 25 °C (30 RH) almost no hydration at all was found with the 70 g samples. This strongly

motivates the combination with an EAHP system, with hydration according to the suggested system concept.

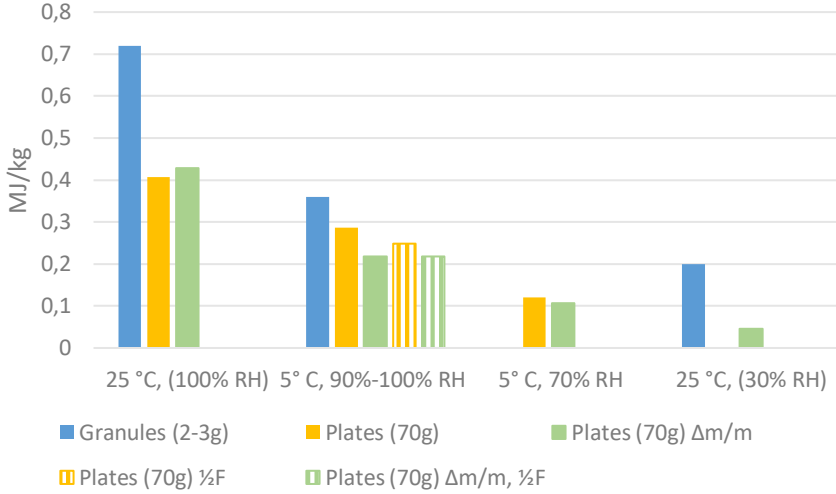


Figure 17. Heat storage capacity during the hydration reaction with samples with a few grams granules (blue) and 70 g plates. $\Delta m/m$ stand for mass increase ($\Delta g/g_{sample}$). For the plates samples the values are calculated from temperature data (yellow) and from the $\Delta m/m$ (green).

6.2.1 Water vapour sources

The energy/water vapour source for the chemisorption is an important point of consideration and are commonly mentioned to be showers, cooking, watering plants etc. The water vapour in outdoor ambient air can also be seen as energy/water vapour source, considering that while using a TES sorption system, the specific humidity (SH) of house ventilation systems inlet (ambient) air can be higher than that of the outlet air. Results of this work show that this is possible with the suggested TES system set up at a Helsinki location, however, the sorption must still be efficient enough (material not too far converted) and the outdoor air not too dry (eg. very cold days). Following the same pattern, outdoor air SH becomes an increasingly important water vapour source when using a standard open TES system with highly ad-/ab-sorptive (and expensive) material, such as zeolite.

The heat source for water vaporization (shower, cooking, watering plants) is usually electricity: directly or via a heat pump. In modern houses a fraction of the heating energy (in this case geothermal heat) is used to produce water vapour (Zevenhoven et al. 2018). Interestingly, the heat source of outdoor air (water vapour indirectly transferred to the exhaust air) water vapour generation for the sorption reactor of, is fully renewable (solar). However, all

usable energy in form of chemisorbing water vapour (from activities listed above) is relevant for increasing the indoor RH. Collecting the energy (chemisorption or condensation) improves the heating efficiency and optimal use of the energy/water vapour available. This energy can also be partly collected within the ventilation system with an efficient heat exchanger (heat from outlet air to inlet air) in cases where the outdoor air RH is close to the dew point.

Condensation of the water vapour (generated indoor) on the heat exchanger would heat up the inlet air, although below 0°C the condensation of water might result in freezing of the surfaces, resulting in decreased heat conductivity and efficiency. This is a common problematic issue and is usually resolved by shutting down the ventilation, by-passing or electrical heating to melt the ice. Even a less efficient sorption of the outlet/exhaust air moisture would resolve this issue, not only providing heat from a sorption reactor but also by considerably increasing the heat exchangers efficiency during the most important period, when the outdoor temperatures are below 0 °C.

6.2.2 Hydration kinetics, heat rate and serial reactor configurations (Paper V and VI)

In section 5.3, the set-up for testing kinetics and measuring the enthalpy of the NQ + silica gel sorption reactions was described. As mentioned in earlier the objective was to produce data on the kinetics depending on the conversion and the enthalpy of the chemisorption reaction.

The kinetics of the chemisorption reactor were shown to give a larger heat output in the beginning at lower conversion (hydration) levels of the reaction (R8). Operation at high(er) initial hydration conversion levels resulted in a lower heat output. The decreasing heat output and increasing conversion in terms of mass increase (due to chemisorption) over time is shown in Figure 18, in agreement with studies by others (Hongois et al. 2011, Zondag et al. 2013).

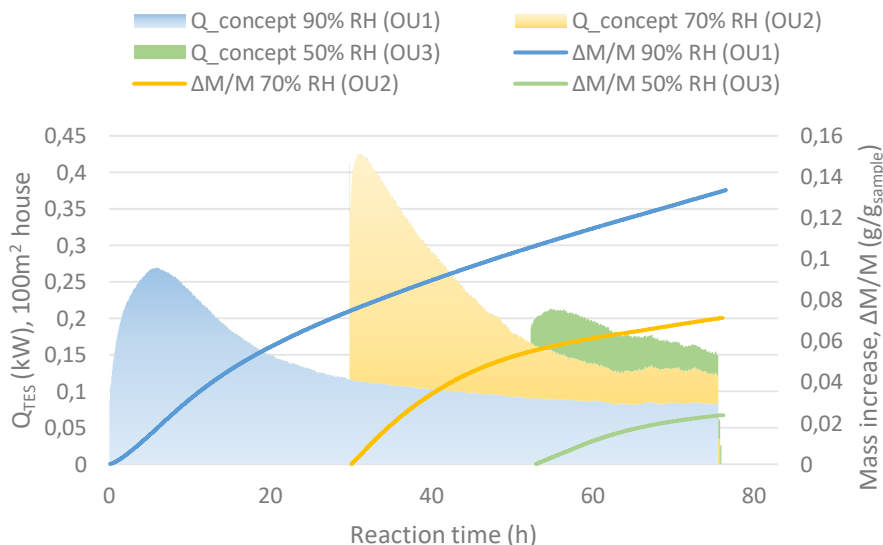


Figure 18. Q_{TES} shows the heat output for a 100 m² house with minimum ventilation and $\Delta M/M$ (g/g_{sample}) stand for the mass increase compared to the initial mass (as dehydrated) of the sample (Paper VI).

The uneven heat output may levelled out by dividing the reactor into several units which would be connected in series. It can be mentioned that when operating at high hydration conversion levels, the reactor outlet gas is not dried completely. A lower the heat output results from less water vapour chemisorbed. The still humid air is nonetheless suitable as inlet air for another reactor unit with a lower TES material hydration conversion grade. Serial operation according to Figure 19 would level out the reactor as shown in Figure 18 with three reactor units connected in series. The RH variations between the units shown at reaction time 55 h in Figure 6 is shown in the scheme shown in Figure 19.

In many cases a very large reactor would resolve this by providing enough unreacted material, but for a STES system the size should be minimized. Obviously, the cost and size are important for seasonal operation.

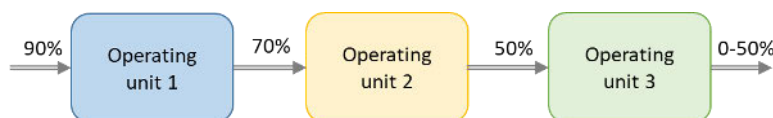


Figure 19. Schematic graph over the operating units connected in serial and the relative humidity (RH) of the inlets/outlets (Paper VI).

A more complex combination of reactors as in Figure 19 to produce a suitable heat output for heating systems, motivated making hourly-based simulations for the heating concept over a whole year (heating period and charging/ desorption period) and compare the results with the performance of a single unit TES reactor system – as described below.

6.3 Simulations and concept system limitations

The operation of the STES reactor and its maximum heat output depend on two major parameters being the relative humidity (RH) and the conversion grade, which both are highly variable. The outdoor RH (obviously indoor as well) varies with the weather (eg. sunny or rainy), although primarily the outdoor temperature affects the indoor RH. Regarding the TES material hydration conversion grade, relatively unconverted material (DNQ) can be made available by the dividing of the reactor into units and connecting them in serial, as presented in (Figures 18 and 19).

However, the outdoor RH cannot be controlled, depending completely on the local weather of the whole heating period. This strongly affects the heat output of the STES that aims at substituting the use of an external/extra heat source (usually the electrical heating resistance) supporting EAHP. The weather may vary from dry cold to frosty/humid around 0 °C or, depending on the month, extreme cold. Basically, to determine the applicability to the STES reactor, simulations have to be made for a whole year at the building location. In paper VI, simulations were reported using weather and solar radiation data from Helsinki, Finland (see Fig 20) located at the coast of the Baltic Sea. Additionally, another simulation (see Figure 21) with data from Kuopio, Finland (not earlier published data) was made, which is for 400 km northeast of Helsinki and 300 km from the shore, being colder and drier in the winter. Detailed data is shown in Table 5. House size and insulation specification are described in Table 3, heating system data in Table 4, respectively.

Simulations of the first location considered 1, 4 and 5 (serial) reactor units, respectively, following the procedure with serial reactor units described in the previous section. Compared to Figure 18 based on controlled laboratory tests, the simulated heat outputs are quite well levelled or evened out, due to larger reactor volumes relative to the airflow and smoother starts (for taking into use) of the following reactor (n+1) unit in order.

6. KEY FINDINGS

Table 3. House size and insulation data.

Input	U (W/m ² ·K)	Area (m ²)
Roof	0.09	50
Apartment floor	0.16	50
Wall (neighbour)	0	100
Wall (outside)	0.17	35
Windows	1	15
Average U	0.13	
Total wall area		250

Table 4. House heating and ventilations system data (Paper VI)

Residential time air	2	h
η_{th_HRV} , efficiency	85%	kW _{inlet} /kW _{outlet}
Q _{EAHP} max *	~ 1.5	kW
Q _{TES} max (theoretical)	0.67	kW
Hot water usage**	0.8	kW

*without condensation from exhaust air, higher heat output with condensation.

**Average heating effect required. The total heating effect of hot water usage during the day (19.2 kW).

6. KEY FINDINGS

Table 5. Reactor set up and result from the simulations (Paper VI, excluding Kuopio).

Simulation data	unit	Hki1 1R	Hki2 1R	Hki3 3OU 4R	Kuopio 3OU 4R
n _{OU} , # of operating units	#	1	1	3	3
n _R , # of reactor units	#	1	1	4	4
OU ₁	kWh			426	367
OU ₂	kWh			43	29
OU ₃	kWh			159	139
Q (used capacity)	kWh	500	447	628	536
Q _{Out} (after HEX)	kWh	449	358	534	456
Q _{HC} heat Capacity available*	kWh	-	-	760	660
Used					
Q/ΔH Chemical capacity	kWh/kWh	0.66	0.81	0.82**	
Max Conversion grade***	mol/mol			0.8****	0.8
ΔH Chemical capacity	kWh	760	550	760	660
Reactor size	ton	11.3	8.2	11.3	9.8

* The heat capacity available at when a certain max conversion grade is used.

** Due to recharging of the TES reactor during spring, the used chemical capacity can be higher than maximal conversion grade.

*** The reactor unit is available for heating until the max conversion is reached.

**** The reactor unit is not used after the conversion reached 0.8 (or 20% left of the capacity)

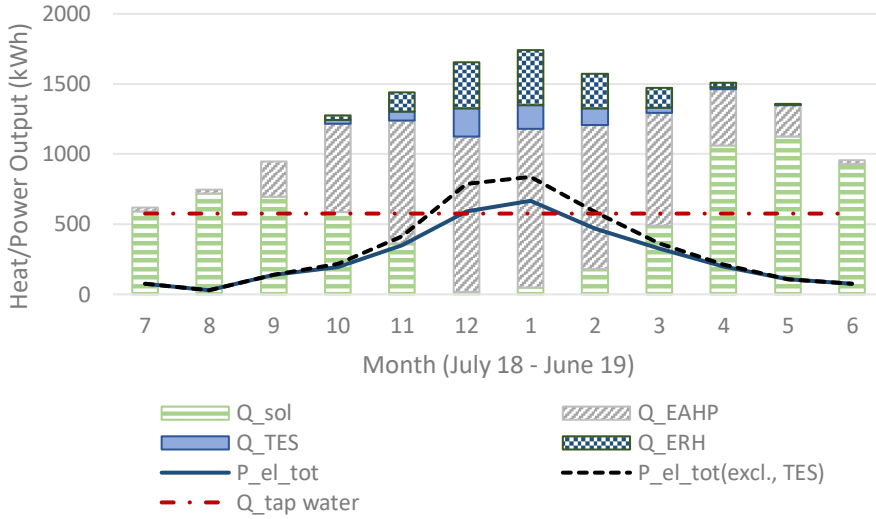


Figure 20. The sum of heat output (Hki3) for all heat sources and electricity consumption on monthly basis (Paper VI).

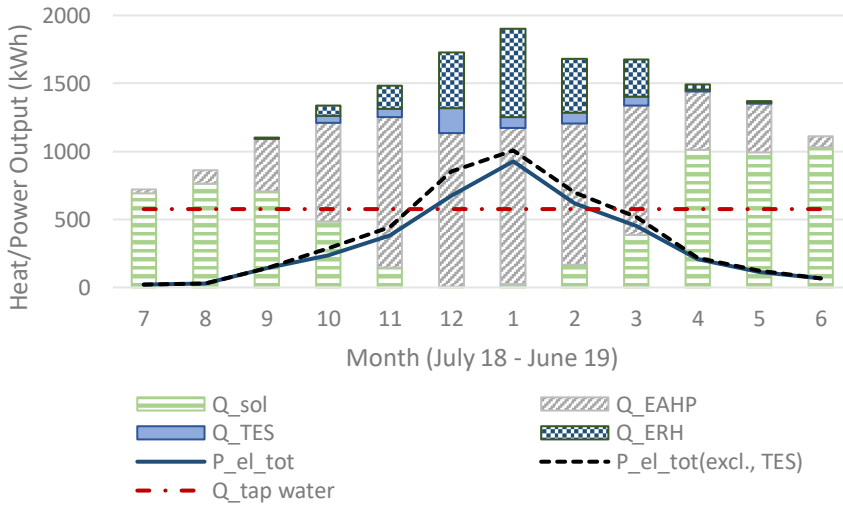


Figure 21. The sum of heat output in Kuopio for all heat sources and electricity consumption on monthly basis.

Despite of the longer heating period in Kuopio, a STES reactor with four units delivered less total heat (Q_{TES} , kWh). The very low temperatures and slightly drier air compared to Helsinki resulted in a lower heat output. This resulted in lower heat output in January and February compared to December (and

compared to January and February for case Hki3), although the extra (supporting EAHP) heating demand (electrical resistance heating, $Q_{ERH} + Q_{ETS}$) is in the same order as for December, as shown in Figure 21.

In these simulations, the first operating unit in use at a given moment is taken out of use when 80% (maximal conversion grade) of the material is hydrated, allowing an unconverted reactor unit to start with the two other reactors to become active later in order (n-1). One approach to improving the reactivity is to decrease the maximal conversion grade to 70% or 60%. A few tests done showed that this would increase the effectively reactive water vapour for the reactor and thus the availability of heat during the heating period. This would increase, however, the amount material required per kWh, decreasing the overall heat storage capacity or requiring a larger system. Another option would be to use the reactors later in the spring (operating from 60 to 80% hydration) when the weather is not very cold and the indoor and outdoor RHs are higher. However, occasional dryness in the spring may be a challenge for this idea.

Thus, it can be concluded that a more dry situation (dictated mainly by the weather) decreases the heat output, which can partly be increased by allowing a lower maximal conversion grade, however decreasing the effective heat storage capacity.

For this system/concept it is noticeable, that the maximum heat output is theoretically limited by the water vapour in the exhaust air and the STES reactor size cannot be increased to fully replace an electrical resistance heating. Considering that in the simulations only 1/3 of the electrical resistance heating could be covered by the STES reactor, what other measures are possible to substitute the electrical resistance heating with STES?

From the economical point of view, the decrease of 639kWh electricity consumption would decrease 80-200 euro per year depending on the area. A long payback time, such as 10 years, would allow up to 2000 euro cost for the STES system. The EAHP investment of around 5000 euro and solar collectors are not included as the payback time is reasonable, usually under 10 years, although strongly varying on the circumstances. The price of the magnesium carbonate is very low compared to silica gel that start from 100e/ton, being the main cost of the reactor material. The material cost for 5.65 tonnes NQ and silica gel each, would be more than 600 euro. This would result in a reactor system cost of more than 1000 euros for a small house, were a maximum price around 2000 euro would be appropriate. The system would be more feasible in larger buildings, considering that material price would probably be larger than the system prices, due to its simple set up.

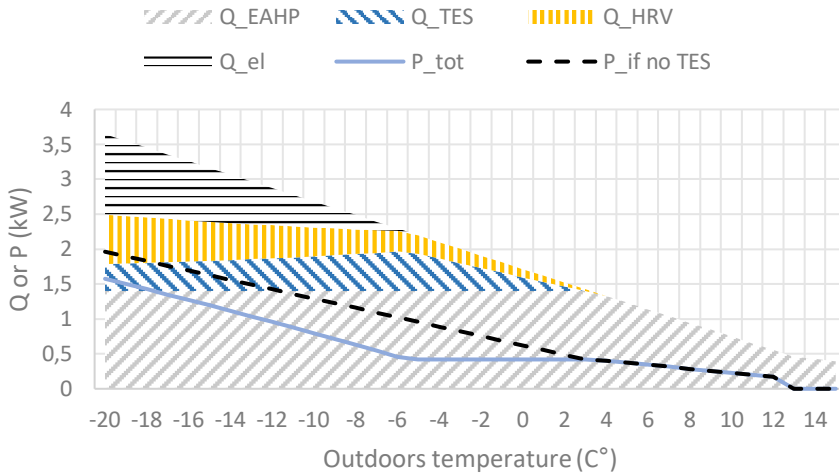


Figure 22. Heat sources heat output and power required with and without TES at various outdoor temperatures according to the concept. Water vapour pressure consists of the 100% RH at outdoor temperature and moisture that is generated in normal in-house living conditions (showering, plants etc.) (Paper VI).

The house/apartment type (detached house) considered in the simulations has an assumed heat loss given by $U = 0.13 \text{ (W/m}^2\cdot\text{K)}$. Shown in Figure 22, the demand of extra heat supporting the EAHP starts around 3°C and the STES reactor and electrical resistance heating (ERH) steps in at -6°C . The system could be applied in an apartment house that typically has a lower wall area per volume and where people are (in most cases) living in a smaller space, generating more water vapour per m^3 air. All this mentioned, the EAHP and STES would then cover a larger fraction of the heating demand, and the demand for ERH would be considerably decreased.

At least one heat pump manufacturer (nilan.fi) provides a new type of product that uses both exhaust air and geothermal heat, being a good option to combine with the thermo-chemical energy storage, as in this concept. Under Nordic climate conditions, the minimum design temperature before electrical resistance heating (or other extra heating source) needs to step in is at around -5°C (eg. geothermal heat), and not at $+3^\circ\text{C}$ as in the calculations given here, which could be reached with the measures mentioned above.

7. Conclusions

7.1 Magnesium extraction from rock.

For serpentinite, extraction efficiency of magnesium from serpentinite at around 75-80 % was achieved using ammonium bisulphate (ABS) solvent in an aqueous/solid reactor (Paper II). Substituting half of the ABS with ammonium sulphate to use less energy requiring regeneration of acidic salt, increased the reaction time from 2 h to 3 h for sufficient (> 75%) magnesium extraction. This is obviously better than the extraction efficiency of 60-65% obtained with the solid/solid reactor.

Diopside and Mg-hornblende (available in Southern Finland close to a site of significant CO₂-emissions) showed very poor extraction of magnesium, an efficiency of a few percent in the aqueous reactor and under 1% with solid/solid. The best extraction results with aqueous/solid reactor would have a CO₂ binding capacity of 292 kg CO₂/ton (Serp-A 500 km from the CO₂-source) and 260 CO₂/ton (Serp-B, 100km from the CO₂ source) ,while the solid/solid reactor would bind 240 kg CO₂/ton and 207 CO₂/ton with Serp-A and -B, respectively

Finally, choosing the preferable option of these two extraction options may depend on the type and temperature of waste/excess heat that will be available at the site of the CO₂ producer or the nearby industry.

7.2 Seasonal thermal energy storage with magnesium carbonate hydrate

Applying magnesium carbonate hydrate (MCH) for thermal energy storage is sufficient only in form of nesquehonite (NQ). Other crystal forms of MCH are not suitable due to lack of chemical reversibility and/or low ratio of crystal water per mass. However, for sufficiently efficient and useful TES operations with NQ, the following points need to be considered:

- For sufficient hydration, dehydrated NQ is mixed with silica gel (SG) forming a composite material to improve the contact between magnesium carbonate and water vapour, resulting in improved reaction (hydration) rate and conversion levels.
- The dehydrated NQ and SG weight ratio is optimal between 1 and 2 kg/kg MgCO₃·3H₂O/SG.

Presumably it is not sufficient to store heat with MCH without mixing it with silica gel, due to heat/mass transfer limitations during hydration. However, dehydration of MCH is fast and efficient, as the dehydrating NQ (charging step of the thermal energy storage) a few grams sample in 2 hours at 65°C and 90%

converted dehydration was obtained at 50°C. The challenging part is the rehydration step, at lower temperatures where a high RH can still mean a low specific humidity, both resulting in lower heat output per volume humid air.

The STES reactor can operate at high (suitable) RH (when the exhaust air is cooled) when connected to an EAHP system, adding around 22-32% to the heat output of the system. The concept presented in the thesis is motivated by the fact that exhaust air with 5-6 g/kg specific humidity (SH) at 25 °C (30% RH) showed almost no hydration at all. Interestingly, the similar SH cooled to 6-7 °C and 90–95% RH resulted in a heat storage capacity of 0.29 MJ/kg.

Under circumstances of low outdoor temperatures, resulting in low RH in the exhaust air, the concept is suitable for all TES by sorption reactors requiring higher RH, increasing the heat storage capacity. It must still be noted, that the increase of the sample size (scaling up from a few grams on a so-called watch glass to the laboratory pilot amounts deposited on a plastic grid support) gave a TES material with a lower heat storage capacity (shown in section 5.2.2). The reactor should be developed further for better contact (for mass and heat transfer) between the sorption materials giving better heat rate and storage capacity. The effect of extending the residence time could be examined too.

The simulations showed that 1/3 of an auxiliary heat source supporting an EAHP can be substituted with a MCH + silica gel STES reactor in a small (m²) detached house located in Helsinki. The substitution can be higher in larger buildings with lower heat loss per volume, and (in several cases) larger water vapour generation. The simulation at both coastal and inland locations showed that more dry circumstances lower the heat output of the reactor. It can partly be improved by allowing a lower conversion in a reactor unit before switching to an unreacted unit, resulting in lower heat storage capacity.

More importantly, the simulations showed that the dividing the reactor into units in serial order, increases the consistency of the heat output, which also resulting in an increased annual (for STES) heat output of 40%.

The heat output is strongly limited by the specific humidity in the exhaust air, which is the reason why a STES reactor of a reasonable size of a few m³ cannot be increased to entirely replace the electrical resistance heating (or other heating) demand. This limits the heat storage capacity for this concept/process. The maximal heat output depends strongly on relative humidity (RH) and the TES material hydration conversion level. Weather has the largest effect on the outdoor and also indoor RH and hydration conversion level can be controlled optimally by operating the reactor as serial units described in section 5.2.2.

The indoor water vaporisation (shower, cooking, plants drying) heat source for houses / buildings (not connected to district heating) is usually electrical resistance or as heat pumps. However, in case of sufficient sorption, the part of

water vapour in the exhaust air generated outdoors, can be considered as renewable energy.

7.3. Future work

For the extraction step in the CCSM process life cycle assessment (LCA) calculations and more detailed energy calculations for the newest ÅA-route alternatives would add valuable information. This would give scientific data for the decisions between two extraction alternatives.

The TES system concepts presented are limited to space heating close to the customer. The MCH will be produced in abundance amounts in the future when CCSM will be implemented in full scale. For the large amounts of MCH, several other heating concepts using the sorptive material could be developed to boost efficiency of various heating and cooling systems.

A natural continuation for the MCH TES research presented would be an LCA for the process and comparing the carbon footprint to other TES materials and heat solutions. However, to ensure these calculations the durability of the material during many heating cycles could be determined. This includes optimising the degradation of NQ to HM by minimising the amount of CO₂ gas during dehydration/desorption.

The lost (lower) heat storage capacity of the scaled-up test in the laboratory pilot should be investigated further. One solution might be the earlier mentioned improved contact between the material and the water vapour in the air. Reaching the heat storage capacity obtained in the small scale tests (few grams) would make MCH chemically competitive with other sorption material with a low price.

Currently, the heat storage capacity, the temperature range of operation below 100°C, and the low costs for raw materials combined with the CO₂ emissions mitigation the MCH production embodies give TES based on MCH several advantages. International policies on zero-emission energy technology and CO₂ emissions mitigation will, when implemented, give further support.

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Rickard Erlund

Production and Testing of Magnesium Carbonate Hydrates for Thermal Energy Storage (TES) Application

För att uppnå målen i Parisavtalet (Förenta nationernas klimatavtal) om minskade koldioxidutsläpp är alla fungerande och genomförbara åtgärder viktiga, inklusive teknik för förnybar energi och koldioxidavskiljning och lagring (CCS). Utgående från det faktum att geologisk koldioxidlagring inte är möjlig i Finland eller Östersjön, är koldioxidavskiljning och lagring genom mineralisering (CCSM) Finlands ända CCS alternativ. I denna avhandling ingår både forskning inom CCSM och produktion och användning av dess slutprodukt, magnesiumkarbonathydrat (MCH) för lagring av termisk energi (thermal energy storage, TES). Senare delen av avhandlingen behandlar utvecklingen av en process som använder MCH som ett TES-material inklusive termisk systemmodellering och simulering med hjälp av de experimentella resultaten. TES kan utöka användningen av värme som produceras i förnybara källor som inte tillgodoser efterfrågan på en gång. Genom att utveckla ett material av CCSM-karbonatprodukten som förmodligen finns tillgängligt i rikliga mängder i framtiden, motiveras CCSM ur både ekonomisk och miljömässig synvinkel.

To reach the goals of the UN Paris climate agreement on reduced CO₂ emissions, all feasible measures are important, including renewable energy technologies and carbon capture and storage (CCS) technologies. Considering that geological CO₂ storage in Finland or the Baltic Sea region is not possible, the only option in/near Finland is carbon capture and storage by mineralisation (CCSM). This thesis covers both research of a CCSM process and production and use of the end product, magnesium carbonate hydrate (MCH) for thermal energy storage (TES). The development of a process using MCH as a TES material includes thermal system modelling and simulations using the experimental results. TES can expand the use of heat produced by renewable sources that do not meet the demand at the same moment. Developing a material out of the CCSM carbonate product that is useful in the future motivates CCSM from both economic and environmental points of view.



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