Martin Slotte

Two Process Case Studies on Energy Efficiency, Life Cycle Assessment and Process Scale-up

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M.Sc (2011) in technology (chemical engineering), Area of specialization: thermal and flow engineering and process design and systems engineering. During 2010-2011 worked as a Development engineer at Wärtsilä Oy before working as a researcher at the Laboratory of Thermal and Flow Engineering at Åbo Akademi University, under the Graduate School of Energy Efficiency and Systems (GSEES) (2012-2015) and EU FP7 project BUONAPART-E (2012-2016).

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Preface

This work has been conducted at the Thermal and Flow Engineering Laboratory at Åbo Akademi University (ÅAU). The work has mainly been funded by the Graduate School of Energy Efficiency and Systems (GSEES) (2012-2015) and EU FP7 project BUONAPART-E (2012-2016), and by a scholarship awarded by the Rector at ÅAU.

After finishing my M.Sc. degree I had a chat with my then supervisor, Ron Zevenhoven, during which he mentioned that I would probably have what it takes to do a Ph.D. At this point I went to work for Wärtsilä Finland Oy in the same group that I worked with while I wrote my M.Sc. thesis. A couple of years later, the idea of doing a Ph.D. felt right. By chance I saw an ad for Ph.D. candidates within the Graduate School of Energy Efficiency and Systems (GSEES) financed by the Academy of Finland and coordinated by Aalto University in a newspaper. One of the positions open for applications was at Åbo Akademi University with Ron Zevenhoven as supervisor. I took the opportunity and contacted him. After talking for a while, we both felt comfortable and he gave me support in writing my application for the Ph.D. candidate position. I was accepted by the GSEES and began my studies in January 2012. My area of research was the energy optimization of the carbon capture and storage by mineralization (CCSM) process being developed in the laboratory. At the same time as I started, another project had also started which would become part of my work. It was the EU FP7 BUONAPART-E project which had the goal of scaling up a metallic nanoparticle production process. The final envision scale was to be able to produce 100 kg/day nanoparticles. In this project, I would be focusing on the energy efficiency of the process and on performing Life Cycle Assessments.

I would like to thank my supervisor professor Ron Zevenhoven for all the help and guidance he has given me during my time as a Ph.D. candidate. Without those few words at the end of my M.Sc. studies I would never have thought about doing a Ph.D. I would also like to thank my article co-authors; Dr Ines Romão who was of great help in the beginning when I was trying to learn how the CCSM process works and how to use Aspen Plus v7.2 and HSC 5.11 software I would need and professor Greg Metha who was my supervisor during my stay at the University of Adelaide where he helped me figure out what various chemicals can be used when producing nanoparticles through a wet chemical synthesis and how those chemicals are produced. In addition, I would like to thank everyone at the Laboratory of Thermal and Flow Engineering, Vivéca Sundberg, Alf Hermanson and Professor Henrik Saxén for helping with practical things such as travel and reporting issues as well as

Svensk sammanfattning

Då levnadsstandarden ökar för den ständigt växande befolkningen ökar även trycket på miljön och efterfrågan på resurser. Att göra saker på samma sätt som de alltid har gjort är ohållbart. Nya processer måste uppfinnas och utvecklas som kommer att sänka miljöpåverkan och samtidigt livskvaliteten för alla. När dessa nya processer har visat sig fungera i liten skala i laboratorier måste de skalas upp till industriell storlek. Medan man skalar upp en process är det viktigt att ta hänsyn till begränsningar som uppkommer av resursanvändning, såsom energi och materialresurser samt påverkan dessa har på miljön. Att förbättra energieffektiviteten av en process är ett mycket bra sätt att minska användningen av primärenergi samt att minska processens miljöpåverkan. Detta är också en viktigt för energiekonomin, det minskar på kostnaderna för energi som används, och energieffektivitet anses ofta vara en energiresurs eftersom det bidrar till att minska den primära energianvändningen. Förutom de uppgifter som traditionellt hört till när processer har skalats upp bör även energieffektivitetsberäkningar och livscykelanalys (LCA) beräkningar och utvärderingar utföras. Dessa verktyg kan användas för att visa var den studerade processen bör förbättras för att få en mera energieffektiv och miljövänlig process. Verktygen kommer också till hjälp då de gör det lättare att jämföra den studerade processen med redan befintliga processer.

Två typer av processer har studerats i denna avhandling: två processer för avskiljnings, användnings och lagrings av koldioxid (CCUS) med hjälp av CO_2 mineralisering (CCSM) och en process för tillverkning av metalliska nanopartiklar med hjälp av elektrisk båg- eller gnistaurladdning. CO_2 mineralsekvesteringsprocesserna som har studerats i denna avhandling är varianter av en process. Den ena processen har utvecklats en längre tid vid Åbo Akademi och som på senare tid börjat kallas "ÅAU route for CCSM" eller ÅAU rutten för CCSM och en nyare variant som kallas "ÅAU alternative route for CCSM" eller den alternativa ÅAU rutten för CCSM. Den första varianten av processen involverar extraktion av magnesium från ett magnesiuminnehållande mineral, serpentinit, och konvertera den till $Mg(OH)_2$, som därefter karbonatiseras med CO_2 i en rökgas i en trycksatt fluidiserad bäddreaktor vid förhöjd temperatur. Den andra processvarianten involverar de samma processtegen som första varianten där magnesium extraheras ur ett magnesiuminnehållande mineral men konverteras till $MgSO_4$ som sedan karbonatiseras i vattenlösning med CO_2 i en rökgas vid atmosfäriskt tryck och omgivningstemperatur. Nanopartikelproduktionsmetoden har studerats av ett konsortium av tjugoen parter inom EU och Norge, i ett FP7 EU-projekt.

Processerna har evaluerats för energianvändning och miljöeffekterna av en uppskalning. De tre processerna är nya, med målet att skala upp dem från laboratorieskala till full industriell tillämpning. Ett av verktygen som valts för att analysera energieffektiviteten och för optimering av energianvändningen och integration av mineral karbonatiseringsprocesserna var exergi analys. Detta verktyg användes också för att studera energieffektiviteten i nanopartikelnproduktionsprocessen. Exergi analys är baserad på termodynamikens andra lag, och ger möjlighet att beräkna mängden nyttigt arbete eller maximal effekt som kan utvinnas ur en viss energiform. LCA används för at utvärdera miljöaspekterna av en process eller produkt under hela dess livscykel, från utvinning av de resurser som krävs fram tills produkten återvinns eller deponeras. LCA är ett användbart verktyg eftersom det ger stöd i beslutsfattning om hur en process eller produkt påverkar miljön. Processen för att genomföra en LCA-studie har standardiserats av Internationella standardiseringsorganisationen (ISO), i serien ISO 14040. Aspen Plus® (7.2), MS Excel 2010 och HSC användes för att modellera CCSM processen och för att beräkna exergierna av processflödena under medan exergierna för nanopartikelproduktionsprocessen beräknades utan någon särskild programvara. SimaPro (7.3) programvara valdes för LCA-studierna.

CCUS/CCSM processerna har tidigare studerats av flera forskare och de optimala värdena för processvariabler och processinställningar har identifierats. Genom att använda exergi analys för att utvärdera energieffektiviteten i den äldre processvarianten när den kombineras med en kalkugn har processens värmeekonomi förbättrats med drygt 30 %. Den optimerade processen kunde fånga och binda 187 kg CO_2/h vid bearbetning 550 kg serpentinit per timme med 486 MJ värme och 166 MJ el, respektive. Detta motsvarar 2,59 MJ och 0,88 MJ per kg CO_2 bundet. LCA studien utfördes som en "från vagga till porten" studie och den funktionella enheten för studien var sekvestering av ett kilogram CO_2. Resultaten av LCA-studien visar att processen har negativa växthusgasutsläpp, genom att sekvestera ett kilogram CO_2 minskar utsläppen av CO_2 med 0,445 kg. Den främsta källan till utsläpp av växthusgaser från ÅAU route CCSM processen är kompression av rökgasen till 80 bar(g) som krävs för snabb karbonatisering. Även om utsläppen av växthusgaser är negativa för processen måste de andra effekterna på miljön beaktas. Processen har en negativ inverkan på miljön i tre av fyra påverkningskategorierna: den mänskliga hälsan (2,4·10^{-07} DALY), ekosystem kvalitet (0,0211 PAF m^2 år) och utarmning av resurser (9,24 MJ primärenergi). För den alternativa processen visar LCA studien att genom att sekvestera ett kilogram CO_2 minskas utsläppen av CO_2 med 0,74 kg. Miljöpåverkan i de tre andra påverkningskategorierna är

1,31·07 DALY, 0,014 PAF m² år och 4,24 MJ primärenergi. The största källan för växthusgasutsläpp (~30 %) är transporten av serpentinit till CCSM anläggningen. Om denna miljöpåverkan är acceptabel eller inte är en fråga som inte kommer att diskuteras i denna avhandling.

Nanopartikeltillverkningsprocessen studerades och optimerades först i laboratorieskala och skalades upp senare till pilotskala med syfte att producera flera kilogram nanopartiklar per dag. Uppskalningen av processen gjordes genom parallellisering av flera OSU enheter optimerade i laboratorieskala till en större anläggning. Experimentell data från både laboratorieskala och pilotskala samlades in tillsammans med värmemätningar och analyserades med hjälp av exergianalys. Det visade sig att nästan all effekt som matas till en OSU eller ett mOSU system lämnar systemet i kylvattnet istället för att skapa partikelytenergi. När man jämför de uppmätta energianvändningarna med den termodynamiska minimienergin som krävs för produktion av nanopartiklar är det uppenbart att processen inte är mycket energieffektiv eftersom processen kräver flera storleksordningar mer kraft för att producera de nanopartiklar än vad det termodynamiska minimumet skulle indikera. För t.ex. koppar nanopartiklar med en diameter av ~ 50 nm var den uppmätta specifika elförbrukningen ~ 250 kWh/kg, medan det beräknade minimumet var 0,06 kWh/kg. Små installationer med färre och kortare rör har en klar fördel jämfört med större installationer så som mOSU installationer ty den ökade rörmängden och rörlängden leder till ökade materialförluster, vilket i sin tur leder till en högre livscykelpåverkan. Optimering av flödesprofilen i rörsystemen och direkt minimera av rörsystemen kan materialförlusterna minimeras vilket i sin tur leder till en signifikant förbättrad insamlingsgrad av nanopartikel produkt och därmed lägre miljöpåverkan. Kylsystemet bör byggas på ett sådant sätt att värmen kan användas som sådan eller som fjärrvärme eller liknande användningsmål med hjälp av en värmepump. Förutom en något lägre produktinsamlingsgrad presterar en mOSU installation mycket lika de mindre OSU installationerna och därför kan man dra slutsatsen att en effektiv strategi för att skala upp nanopartikel produktion upp är att parallellisera flera OSU.

Baserat på de förbättringar som möjliggjordes för både de studerade processerna som möjliggjordes genom utvärdering av energieffektiviteten och livscykelanalys i samband med uppskalningen metodik verkar det som om dessa metoder är giltiga och bör användas i andra skala upp processerna. Även om mognadsgraden för båda processerna har förbättrats under arbetet som rapporteras i denna avhandling är varkendera tillräkligt mogen för full industriell tillämpning. Tillverkningsprocessen för nanopartiklar är mer mogen eftersom

den har testats i pilotskala. Den befintliga produktionstestenheten som ligger i Duisburg-Essen, Tyskland, är av pilotskala och är drygt 8 % av den slutliga industriella skalan. Detta skulle ge en teknisk mognadsgrad (TRL) av 7. Pilotanläggningen kan producera upp till 70 g/h medan den tänkta CCSM piloten skulle behandla över 500 kg av serpentinit per timme och fånga 180 kg CO_2 per timme. CCSM processen är i skrivande stund på TRL-4 och på väg mot TRL-5. Processen har testats grundligt i laboratorieskala som en satsvis process med syntetisk rökgas men en enhet som fungerar som en kontinuerlig process som startar med utvinning av magnesium och slutar med karbonatisering av $Mg(OH)_2$ (eller $MgSO_4$) har fortfarande inte byggts. Att få finansiering för byggandet av den mycket större CCUS pilotanläggningen har hittills visat sig vara svårt, främst på grund av kostnaderna för CO_2-utsläpp inom det europeiska handelssystemet (ETS) för CO_2 gör CCSM ekonomiskt ointressant, oberoende av marknadsvärdet för de fasta produkterna från CCSM.

Abstract

As the standard of living increases for the ever growing global population, the pressure on the environment and the demand for resources also increase. Doing things the same way as they have always been done is unsustainable. New processes need to be invented and developed that will lower the impact on the environment while still making life better. Once these new processes have been proven to work on a small scale in laboratories, they need to be scaled up to industrial size facilities. While performing the scale-up it is important to consider the limitations of resource use, such as energy and materials, as well as the impact the use of the resources has on the environment. Improving the energy efficiency of the process is a very good way of reducing the use of primary energy as well as reducing the environmental impact of the process. This is also an important component of the energy economy, reducing the cost for energy used, and often energy efficiency is considered to be an energy resource, as it helps reduce the primary energy use. In addition to the tasks traditionally related to process scale-up, energy efficiency calculations together with life cycle assessment (LCA) should be performed. These tools can be used to show where the studied process needs to be improved in order to obtain a more energy efficient and environmentally friendly process. The tools will also help as they make it easier to compare the studied process to already existing processes.

Two types of processes have been studied in this thesis: two carbon capture, utilization and storage (CCUS) by means of CO_2 mineral sequestration (CCSM) processes and a process for production of metallic nanoparticles (NP) using electrical arc or spark discharge. The CO_2 mineral sequestration processes are variants of one process. The first variant has been developed for a longer time at Åbo Akademi University and is often called the ÅAU route and a newer alternative which is called the ÅAU alternative route. The first process variant involves extraction of magnesium from a magnesium containing mineral, serpentinite, and converting it to $Mg(OH)_2$ which is then carbonized by flue gas in a pressurized fluidized bed reactor at elevated temperature, while the second variant also involves the extraction of magnesium from the same mineral but converting it to $MgSO_4$ and with carbonation taking place in an aqueous solution at ambient temperature and pressure. The nanoparticle production method was studied by a consortium of twenty-one partners within the EU and Norway, in an FP7 EU project. The processes have been studied for the energy use and environmental impact of scale-up. All three processes are new, with the goal of taking the scale beyond lab-scale and aiming for full industrial

application. One of the tools chosen to study the energy efficiency and for the optimization of the energy use and integration of the mineral carbonation process was exergy analysis. This tool was also used to study the energy efficiency of the nanoparticle production process. Exergy analysis is based on Second Law of Thermodynamics, and gives the possibility to calculate the amount of useful work or maximum power that can be produced from any given energy form. LCA is used for evaluating the environmental aspects of a process or product over its entire life cycle, from the gathering and extraction of the necessary resources to the end of the lifetime of the product when it is recycled or landfilled. LCA is useful as it gives support in making decisions on how they affect the environment. The process for conducting an LCA study has been standardized by the International Organisation for Standardisation (ISO), within the series ISO 14040. Aspen Plus® (v.7.2), MS Excel® 2010 and HSC (5.11) were used to model the CCUS/CCSM process and to calculate the exergy of the process streams, while the exergies for the nanoparticle production process were calculated without any specific software. SimaPro (v7.3) software was chosen for the LCA studies.

The CCUS/CCSM processes have been studied by several researchers before and the optimum process variables and process setups have been identified. By using exergy analysis to evaluate the energy efficiency of the older process variant when combined with a limekiln, the heat economy of the process has been improved by slightly over 30 %. The optimized process was able to capture and sequester 187 kg CO_2/h while processing 550 kg serpentinite per hour using 486 MJ of heat and 166 MJ of power. This translates into 2.59 MJ and 0.88 MJ per kg CO_2 sequestered, respectively. The LCA study of the CCSM process was performed as a cradle-to-gate study where the functional unit for the study was the capture of one kilogram of CO_2. The results of the LCA study show that the process is greenhouse gas (GHG) negative: by producing one kilogram of $MgCO_3$ the net amount of captured CO_2 is 0.445 kg. The main cause of GHG emissions from the ÅAU route for CCSM process comes from the compression of the flue gas to the required 80 bar(g) for fast carbonation. Even though the emissions of GHGs are negative for the process, there are other impacts on the environment that need to be considered. The process has a negative effect on the environment in the Human health ($2.4 \cdot 10^{-7}$ DALY (Disability Adjusted Life Years)), Ecosystem quality (0.0211 PAF m² yr (Potentially Disappeared Fraction multiplied by area and years)) and Resource depletion (9.24 MJ Primary energy) categories. The LCA study shows that by sequestering one kilogram of CO_2 the net emissions are reduced by 0.74 kg of CO_2. The environmental impact in the other three

categories are $1.31 \cdot 10^{-7}$ DALY, 0.014 PAF m² year and 4.24 MJ primary energy. The main contribution to the GHG emissions (~30 %) is the transportation of the serpentinite to the CCSM plant. If these environmental impacts are acceptable is a subject which will not be discussed in this thesis.

The nanoparticle production process functions on the principle of evaporating metal, either as a wire or pellets, in an inert gas using electrical discharges to supply the energy needed for volatilization. The metal-vapour is cooled and condensed to first form primary particles that then agglomerate into NP. The process was first studied and optimized on laboratory scale and later scaled up to a pilot scale aiming at producing several kilograms of nanoparticles per day. The basic reactor unit was referred to as an Optimized Single Unit (OSU) in which the metal evaporation took place. The scale-up of the process was done by parallelization of multiple OSU units optimized on lab-scale into one larger facility, referred to as mOSU. Collected experimental data from both lab scale and pilot scale was analysed with the use of exergy analysis together with heat measurements. The analysis showed that almost all of the power fed to the OSU or mOSU systems leaves the system as waste heat instead of creating particle surface energy. When comparing this to the thermodynamic minimum energy needed, it is evident that the process is not very energy efficient as it requires several orders of magnitude more power to produce the nanoparticles than the minimum would indicate. For copper NP for example of ~ 50 nm the measured specific electricity consumption (SEC) was ~ 250 kWh/kg, while the calculated minimum is 0.06 kWh/kg. Small setups with less tubing have a clear benefit as the additional tubing in a larger mOSU setup leads to increased material losses, this in turn leading to a higher life cycle impact compared to a smaller OSU setup. Optimization of the flow profile in the tubing and by minimizing the amount of tubing, the material loss inside the tubing can be minimized leading to a significantly improved collection rate and therefore lower environmental impact. The cooling system should be set up in such a way that the heat can be used as such or with the use of a heat pump for example for district heating or some other use. Other than slightly lower product collection rates the mOSU performs similarly as the smaller OSU setups and, therefore, it can be concluded that scaling up the NP production by parallelization of OSUs is a valid approach.

Based on the improvements to both studied process made possible by the use of energy efficiency evaluation and life cycle assessment coupled with scale-up methodology, it seems that these methods are valid and should be used in other scale-up processes. Even though the maturities of both processes have

improved during the work reported on in this thesis, they are both not mature enough for full industrial implementation. The NP production process is closer to maturity, as the process has already been tested on a pilot scale. The currently existing NP production test unit located in Duisburg-Essen, Germany, is of pilot plant scale and is slightly over 8 % of the final industrial scale facility. This would give a technology readiness level (TRL) of 7. The NP pilot process can produce up to 70 g/h while the envisioned CCUS pilot would process over 500 kg of serpentinite rock per hour and capture 180 kg CO_2 per hour. The ÅAU CCSM process is at the time of writing at TRL-4 but heading toward TRL-5. The process has been rigorously tested on laboratory scale in a batch-setup with synthetic flue gas, but a continuously operating process-setup starting from the magnesium extraction and ending with the carbonation of $Mg(OH)_2$ (or $MgSO_4$) has not been constructed. To receive funding for the construction of the much larger carbon capture and storage (CCS) or CCUS pilot has so far proved to be difficult, mainly because the costs of CO_2 emissions under the European trading scheme (ETS) for CO_2, which make CCS/CCUS/CCSM economically unattractive, regardless of the market value of the solid products of CCSM.

Contribution of the author and list of publications

This thesis is based on six scientific publications, numbered I-VI, which can be found at the end of this thesis. A more general perspective of the topics covered in the publications is presented in the introduction of this work.

The author of this thesis is the main author and contributor of five of the six publications listed below as Papers I-II, IV-VI and the second author in one publication, Paper III. For all except Paper III the author performed all the modelling and calculations as well as the necessary literature review in order to perform the modelling and calculations and wrote the majority of the papers.

Paper I
Slotte, M., Romão, I, Zevenhoven, R., 2013, Integration of a pilot-scale serpentinite carbonation process with an industrial lime kiln. *Energy* 62:142-149.

Paper II
Slotte, M., Zevenhoven, R., 2013, Total lime kiln gas compression for CO_2 mineral sequestration. In: ECOS 2013 Proc. of the 26th Int. Conf. on Efficiency, Cost, Optimization, Simulation, and Environmental Impact of Energy Systems; 2013 Jul 15-19; Guilin, China. Paper F005. (peer-reviewed).

Paper III
Zevenhoven, R., Slotte, M., Åbacka, J., Highfield, J., 2016 A comparison of CO_2 mineral carbonation processes involving a dry or wet carbonation step. *Energy* 117:604-611.

Paper IV
Slotte, M., Metha, G., Zevenhoven, R., 2015, Life cycle indicator comparison of copper, silver, zinc and aluminum nanoparticle production through electric arc evaporation or chemical reduction. *Int J Energy Environ Eng* 6: 233-243 (open source).

Paper V
Slotte, M., Zevenhoven, R., 2016, Energy requirements and Life Cycle Assessment of production and product integration of silver, copper and zinc nanoparticles. Submitted after revision to *Journal of Cleaner Production.*

Paper VI
Slotte, M., Zevenhoven, R., 2016, Energy efficiency and scalability of metallic nanoparticle production using arc/spark discharge. Submitted after revision to *Environmental Science Nano.*

Related publications

In addition to the above listed contributions, the author of this thesis has contributed to other publications and reports, conferences and meetings as listed below on the field of carbon capture storage through mineralization and nanoparticle production.

BUONAPART-E, 2014, Release, exposure and safety evaluation on synthesis processes based on electrical discharges, Project deliverable no. 6.3

BUONAPART-E, 2015a, Workshop on Life Cycle Evaluation and Energy Use for Different Production Processes of Nanomaterials. (Turku, Finland, April 2015) Project deliverable no. 6.4

BUONAPART-E, 2015b, Costs and Economic Benefit of Scale-up, Including Environmental Impact, Risk and Energy Efficiency, Project deliverable no. 6.5

BUONAPART-E, 2015c Assessment of the characteristics, impact and benefit of process scale-up to 100 kg/day. Project deliverable no. 6.6

BUONAPART-E, 2016a, PROJECT FINAL REPORT M1-M48 (01.02.2012 – 31.01.2016)

BUONAPART-E, 2016b, BUONAPART-E EU FP7 project website http://www.buonapart-e.eu/ accessed 10.10 2016

Clic / Cleen CCSP project Deliverables:

D510Slotte, Martin; Romão Inês; Zevenhoven, Ron Design and technical feasibility study of a magnesium silicate carbonation demo-plant (2013)

D511 Mattila, H.-P.; Slotte, M.; Said, A.; Zevenhoven, R. BOF slag carbonation in aqueous NH4Cl-solutions: steering product quality in continuous process (2013)

D512 Romao, IS; Grigaliunaite, I; Mattila, H-P; Slotte, M; Zevenhoven, R Water management and separation technologies for serpentinite carbonation and for PCC production from steelmaking slag (2013)

D529 Zevenhoven, Ron; Slotte, Martin; Kotiranta, Tuukka Report on detailed design features for Mg-silicate carbonation demonstration at a lime kiln (2016)

D530 Slotte, Martin; Romão, Inês; Zevenhoven, Ron Integration of a pilot-scale serpentinite carbonation process with an industrial lime kiln (2013)

D547 Zevenhoven, Ron; Slotte, M Selection of dry gas/solid (Mg(OH)2) or wet aqueous (MgSO4) carbonation of lime kiln gas CO2 (2016)

D556 Zevenhoven, Ron; Koivisto, Evelina; Erlund, Rickard; Slotte, Martin; Fagerholm, Mats Updated cost evaluation including a feasible plant design for large-scale magnesium silicate carbonation at a lime kiln (2016)

Zevenhoven, R., Slotte, M., Koivisto, E., Erlund, R. Serpentinite carbonation process routes and integration in industry, *Energy Technology* submitted

Romão, I., Slotte, M., Gando-Ferreira, L.M., Zevenhoven, R., 2014, CO_2 sequestration with Magnesium Silicates - Exergetic performance assessment Chemical Engineering Research and Design – special issue on *Thermodynamics* 92 (2014) 2072-2082 DOI: 10.1016/j.cherd.2014.05.016

Slotte, M., Romão, I., Zevenhoven, R., 2012, Challenges in process scale-up of serpentinite carbonation to pilot scale CPOTE-2012 3rd International Conference on Contemporary Problems of Thermal Engineering, 2012 September 18-20, Gliwice, Poland (peer-reviewed), basis for Paper I

Slotte, M., Metha, G., Zevenhoven, R., 2014, Life cycle indicator comparison of copper, silver, zinc and aluminum nanoparticle production through electric arc evaporation or chemical reduction, In: ECOS 2014 Proc. of the 27th Int. Conf. on Efficiency, Cost, Optimization, Simulation, and Environmental Impact of Energy Systems; 2014 June 15-19; Turku, Finland. (peer-reviewed), basis for Paper IV

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List of abbreviations and symbols

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BUONAPART-E	Better Upscaling and Optimization of Nanoparticle and Nanostructure Production by Means of Electrical Discharges
CCS	Carbon Capture and Storage
CCSM	Carbon Capture and Storage by Mineralization
CCUS	Carbon Capture Utilization and Storage
CO_2	Carbon dioxide
DALY	Disability Adjusted Life Years
ETS	European trading scheme
FP7	Framework program 7
GHG	Greenhouse gas
HSE	Health Safety and Environment
IEA	International Energy Agency
ISO	International Organization for Standardization
KIT-S	Karlsruhe Institute of Technology, Germany
LCA	Life cycle Assessment
LCI	Life Cycle Impact
LCIA	Life cycle Impact Assessment
LED	Light emitting diode
$MgCO_3$	magnesium carbonate
$Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$	magnesium hydromagnesite
$Mg(OH)_2$	magnesium hydroxide
$MgSO_4$	magnesium sulphate
MNL	Metal Nanopowders Ltd., United Kingdom
MVR	Mechanical Vapour recompression
NP	Nanoparticle
OSU	Optimized Single Unit
mOSU	multiple Optimized Single Unit
prOSU	production Optimized Single Unit
PAF	Potential Disappeared Fraction
PP	Polypropylene
SEC	Specific Electricity Consumption
SFE	Surface free energy
TUD	Delft University of Technology, the Netherlands
UDE	Universität Duisburg-Essen, Germany
ÅAU	Åbo Akademi University, Finland

Table of Contents

1. Introduction

The increasing global population and the improving standards of living result in a growing demand for goods, services and energy. During the last century, the primary energy demand has mainly been covered by combustion of fossil fuels such as coal, oil and natural gas. As can be seen in Figure 1, over 80% of the global primary energy demand is covered by the use of fossil fuels. This results in large emissions of CO_2 to the atmosphere, which is believed to be the main cause for climate change and global warming.

World[1] total primary energy supply (TPES) from 1971 to 2014 by fuel (Mtoe)
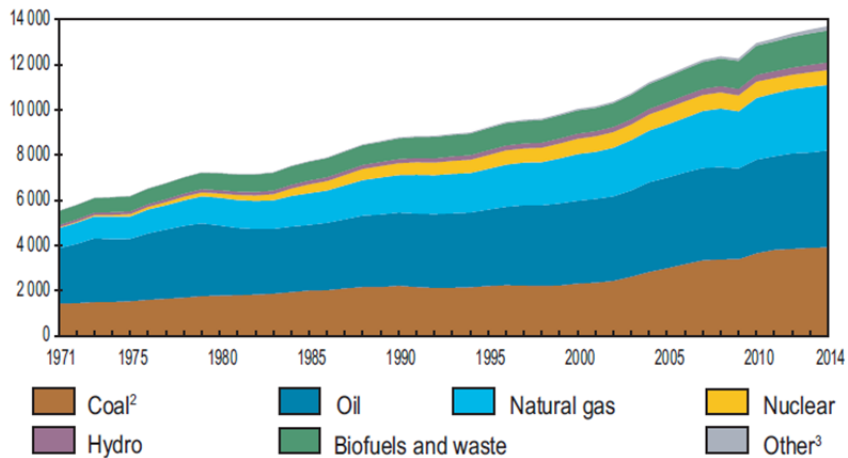
[1] Excludes electricity trade.
[2] In this graph peat and oil shale are aggregated with coal.
[3] Includes geothermal, solar, wind, heat etc.

Figure 1 Global primary energy use. Figure taken from IEA (2016).

In order to keep up with the demand for goods, processes for the production of currently available products and new products need to be scaled up. While scaling up production of an existing product or a new process it is important to consider the limitations of the resources, such as energy and materials and the environmental impact the use of these resources has. An important way of reducing the primary energy use is to improve the energy efficiency of equipment and processes. This is also an important component of the energy economy and often efficiency is seen as an energy resource, as it helps reduce the primary energy use. The potential for improvements in energy efficiency is significant.

In this thesis, two types of processes have been studied from the point of view of the energy use and environmental impact of scale-up. The processes are new processes where the production is taken beyond lab-scale and aim for full industrial application. These processes are: two carbon capture and storage (CCS) by means of CO_2 mineral sequestration (CCSM) and a process for production of metallic nanoparticles (NP) using electrical arc or spark discharge. The CO_2 mineral sequestration processes studied are variants of one process developed at Åbo Akademi University, often called the ÅAU route and the ÅAU alternative route for CCSM, while the NP production method was studied by a consortium of twenty-one partners within the EU and Norway, in an FP7 EU project.

CO_2 mineral sequestration is one CO_2 mitigation method of the carbon capture, utilisation and storage (CCUS) portfolio, and a prime alternative for methods that involve geological storage of CO_2. Here the processes are applied to the flue gas from a lime kiln, which has a relatively high CO_2 content. The production of lime is a CO_2 intensive process and the high CO_2 content in the flue gas makes it highly suitable for CO_2 capture and mineralization. Exergy analysis is used as the tool for the (energy use) evaluation of different compression strategies and process heat integration. Initial tests with the process were carried out in lab-scale with samples of a few grams of serpentinite while over 300 ton per hour of serpentinite would be required for an industrial operation scale, corresponding to approximately 1.0 megaton CO_2 sequestered per year.

Likewise, ways to produce metallic NPs and the scale-up of these processes have seen increased interest as the industrial application of NPs continues to grow. The production of metallic NPs by evaporation of metal using electrical discharge reactors and the integration of the produced particles into commercial products was studied in the European Commission 7th Framework Program (FP7) project "BUONAPART-E" (2012-2016), BUONAPART-E (2016a, b). As part of this, three nanometal-containing products were identified and these production processes were chosen for further assessment of their environmental impact. The three products are NP zinc in polypropylene composite, copper NPs in cooling water and silver NPs in textiles, respectively. The first experiments with the arc/spark process showed production rates of 0.01 g/h while the final experiments showed the possibility to scale up the production rate up to 100 g/h by linear scale-up.
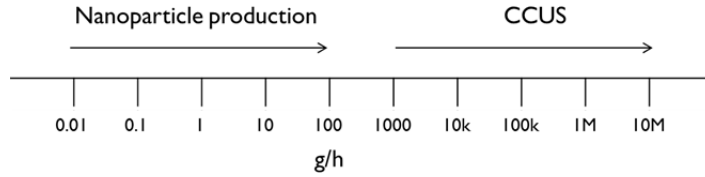
Figure 2 Process scale-up for CCUS and nanoparticle production.

Figure 2 shows the scales of scale-up studied in this thesis. Both processes have been evaluated for scaling them up by four orders of magnitude but the CCUS process is significantly larger, with a starting scale that is five orders of magnitude larger than the starting point for the nanoparticle production process.

The LCA of mineral carbonation has been studied earlier by among others Nduagu et al. (2012), Giannoulakis et al. (2014) and Pasquier et al. (2016). The study by Nduagu et al. (2012) focused on the GHG emissions from a combined coal fired power plant with a CCSM plant, either operating according to the ÅAU route or to the route developed earlier by National Energy Technology Laboratory in the USA (NETL). The authors found that both processes have a negative impact on the GHG emissions, with 483 kg CO_2 avoided per ton CO_2 mineralized using the ÅAU process and 317 kg CO_2 per CO_2 mineralized using the NETL process. The study by Giannoulakis et al. (2014) compared the same processes as the study by Nduagu et al. In addition to evaluating the GHG emissions of the processes, they also studied the other environmental impacts resulting from the CCSM processes as well as the cost of the processes. They found that even though the GHG emissions are reduced with the CCSM processes, the total environmental impact would be larger than for coal or natural gas fire power plants without CCSM. Pasquier et al. compared their process with the same processes studied earlier by Nduagu et al. and Giannoulakis et al. Instead of pairing the CCSM plant with a power plant the authors paired it with a cement plant located in Canada. They concluded that the ÅAU process requires the least amount of heat and power and that the economic feasibility of the process under development in Canada is largely dependent on the market price for $MgCO_3$. Note that none of the studies considered the operation on flue gases directly, as recommended by the process studied here, as was shown by Khoo et al. (2011).

1.1. Objective

In order to pave the way for future industrial application of the studied processes, they need to be evaluated from the viewpoint of their environmental impact and their energy efficiency. Therefore, the objective of the work

presented here was to evaluate the ÅAU CCSM process and the BUONAPART-E NP production process as two case studies, using energy efficiency analysis together with exergy analysis and Life Cycle Assessment.

To fulfil the objective six goals were set:

- The reduction of the heat and power consumption of the CCSM process in order to make the process more feasible for pilot and industrial scale installations, such as power plants or lime kilns.
- The further development of the alternative ÅAU route for CCSM and its comparison to the conventional ÅAU route on both energy efficiency basis and by comparing the environmental impact of both processes.
- The evaluation of technical challenges of scale-up of the CCSM process.
- The evaluation of the energy efficiency of the newly developed arc/spark NP production process.
- The comparison of the environmental impact of NP production by the arc/spark process compared to other more conventional routes.
- The assessment of the environmental impact for the production process of products containing NP produced by the method of interest.

1.2. Summary of publications

Paper I. This work can be seen as a continuation of previous work by Romão et al. with added detail on energy integration and flue gas compression. This results in a significant energy efficiency improvement compared to earlier work. Also, technical challenges of scaling-up are addressed.

Paper II. The work focused on modelling and optimizing the flue gas compression setup required to reach the required 80 bar total pressure for efficient carbonation taking into account the number of compression steps, compression ratios, temperatures and cost. The optimization was done with the help of exergy analysis.

Paper III. The aim of this paper was to report on the production of (hydro-)magnesites by the alternative ÅAU route and to compare the two ÅAU routes. In addition to reporting on experimental findings on the production of (hydro-)magnesite process modelling, thermodynamic equilibrium calculations and exergy analysis were used to compare the two process variations.

Paper IV. The goal of the paper was to calculate the environmental impact of the NP production process developed under the BUONAPART-E project. This was done by modelling the process based on experimental data and calculating the environmental impact using LCA. The LCA results were then compared with LCA results for more conventional wet chemical routes for the production of similar particles. The wet chemical routes were modelled based on published literature data.

Paper V. This paper primarily addresses the environmental footprint of producing metallic NP for use in commercial products. An in-depth assessment was given for the three cases studies that are considered to be the most advanced and well defined at this point after the BUONAPART-E project: 1) use of copper NP as nanofluid dispersion in water for iron- and steelmaking cooling application, 2) use of zinc NP co-extruded into poly propylene (PP) plastic as to enhance flame retarding properties, and 3) use of silver NP in textile application, giving it anti-bacterial properties.

Paper VI. The aim of this paper was to evaluate the LCA of the arc and spark process by comparing the specific electricity consumption for the production of the studied NP, to evaluate the energy efficiency of the process with the help of exergy analysis and finally to assess the environmental impact for the production of three products containing metallic NP produced using the arc and spark processes.

2. Methods
2.1. Energy efficiency

An important way to reduce the primary energy use and the corresponding emissions of processes is to make them more energy efficient. A process is more energy efficient than another if it can deliver more services or products for the same energy input or the same services for less energy input. Energy efficiency is generally improved by adopting more efficient technologies or production processes or by applying other techniques for the reduction of energy loss. Examples of energy efficiency are light-emitting diode (LED) lights compared to incandescent light bulbs. Modern LED lights consume down to ten times less electricity than incandescent light bulbs and modern insulated buildings require less energy for heating or cooling, Osram (2009).

During the last decades, the improvements in energy efficiency have been the most significant change to the global energy system. This has led to the per capita energy consumption in IEA countries decreasing to the same levels as in the 1980s. Even though the per capita energy consumption has gone down, the access to energy and income per capita is at record high levels. This shows that improving energy efficiency is very important and it can be seen as a clean energy source that is domestically available. Investments in energy efficiency within the OECD countries have saved up to 5.7 trillion USD in avoided energy costs since 1990. In addition to saving money, energy efficiency improves energy security for energy importing nations, as less energy needs to be imported while also reducing emissions. It is estimated that up to 40% of the emission reduction needed to reach the goals set for 2050 (in order to limit the increase of the global temperature to less than two degrees centigrade according to the Paris 2015 agreement, UN (2015)), could potentially be achieved by improving the energy efficiency of processes. Even with all these benefits energy efficiency technologies will only be widely used when they are viable economically within their lifetime and when there are no political or social barriers for their implementation.

Energy efficiency is not a specified measure, it is a generic term. Indicators have to be used in order to measure changes in energy efficiency. The most common way of indicating it is by measuring the energy input to a process per ton of product, as shown in equation 1.

$$Energy\ efficiency = \frac{Energy\ used}{Thermodynamic\ minimum\ energy\ input} = \frac{Useful\ output\ or\ product}{Energy\ input\ into\ process}$$

<div align="right">(1)</div>

Other indicators for showing change in energy efficiency have also been devised. These can be divided into four main categories: thermodynamic, physical-thermodynamic, economic-thermodynamic and economic, Patterson (1996). The thermodynamic indicators rely entirely on thermodynamic measurements, while the physical-thermodynamic indicators are hybrid indicators relying on thermodynamic measurements as well as other physical measurements, such as for the case of transporting a certain mass of product a certain distance where the physical unit of measure would be the ton kilometres transported. The economic-thermodynamic indicators work in a similar fashion to the physical-thermodynamic indicators, instead of physical measurements economic factors such as market price that is used together with the thermodynamic measurements for energy input. In the economic indicators, both the output of the process and the energy input are measured in monetary terms.

2.2. Life Cycle Assessment

When improving and optimizing new or old products or services it is important to have a tool for calculating the environmental footprint of said products or services. The need for such tools has been the driving force for the development of methods to better calculate and understand these impacts. The most widely used technique today is Life Cycle Assessment (LCA).

LCA is a tool used for evaluating the environmental aspects of a product or service systematically through its entire life cycle, from the gathering of the necessary resources to the recycling or landfilling of the product after use. It is a tool that gives support to making environmental protection decisions. The process for conducting an LCA study has been standardized by the International Organisation for Standardisation (ISO), within the series ISO 14040 on LCA, ISO (2006).

LCA can be used to help in identifying opportunities for improving the environmental performance of products or production processes in the products' different life cycle stages. It can also be used to help with decision-making in industry, government or non-governmental organizations for setting priorities, designing processes or strategic planning and marketing. However, LCA does not take into account the economic or social aspects of a product or service and, therefore, another tool should be used for that.

An LCA study consists of four phases, and these are:

- goal and scope definition phase,
- inventory analysis phase,
- impact assessment phase, and
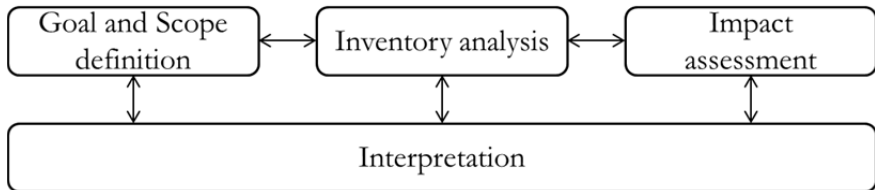- interpretation phase.

Figure 3 Life Cycle Assessment phases under ISO 14040.

In the first phase, the goal and scope of the study are defined. This includes setting the system boundary and deciding on the level of detail to be included. The goal of the study depends on the intended use of the results. The life cycle inventory analysis phase (LCI phase) is the second phase of LCA. In this phase all the input/output data, such as raw resources, energy by type, emissions to air, water and land, which are necessary for the goal of the study, is collected and assessed. This phase can be very complex as it may involve dozens of unit processes in a larger process. Examples of unit processes are extraction of raw material, refining of materials in various primary and secondary processes and transport of materials and products.

The third phase is the life cycle impact assessment phase (LCIA). The purpose of the LCIA phase is to provide additional information in order to better understand the environmental significance of the product or service being assessed. The fourth and final phase is the life cycle interpretation phase. In this phase, the results of an LCI or LCIA are summarized and discussed. For example, the manufacture of a certain product may consume a measured or otherwise known volume of natural gas and in this phase the global warming impact of the use of that gas is calculated. Based on the findings, recommendations and decisions can be made. Figure 3 shows the LCA phases and their relations to each other.

There are cases where the goal set for an LCA can be satisfied without performing all of the four phases and therefore the ISO 14040 standard covers two types of studies: life cycle assessment studies (LCA studies) and life cycle inventory studies (LCI studies), respectively. These types of studies are similar

except that the LCI study excludes the life cycle impact assessment phase of a full LCA study, ISO (2006).

In this work an LCA software: SimaPro 7.3 using the Ecoinvent v2.2, Ecoinvent (2012) database was used to calculate the environmental impact for the different NP production scales. This was done using the IMPACT 2002+ method. In the IMPACT 2002+ method the environmental impact is calculated for 14 midpoint categories, which are then summarized into four damage categories: Human health, Ecosystem quality, Climate change and Resource depletion, Margni et al. (2003).

These four categories take into account different effects: the Human health category takes Human toxicity, Respiratory effects, Ionizing radiation, Ozone layer depletion and Photochemical oxidation. Ecosystem quality in turn takes into account Ozone depletion, Photochemical oxidation, Aquatic ecotoxicity, Terrestrial ecotoxicity, Aquatic acidification, Aquatic eutrophication, Terrestrial acidification and nitrification and Land occupation. The Climate change category takes into consideration emissions causing Global warming, while the Resource depletion category takes into account the non-renewable energy use and Mineral extraction.

These categories are quantified by the following units: DALY, (Disability Adjusted Life Years), for Human health, $PDF \cdot m^2 \cdot year$, (Potentially Disappeared Fraction multiplied by area and years), for Ecosystem quality, kilogram CO_2 equivalents, for Climate change and MJ primary energy for the Resource depletion category. DALY is a measure of overall disease burden which is expressed as years lost due to ill-health, disability or death. PDF is a measure given for species affected by toxins at certain concentrations. CO_2 equivalents are defined as the amount of CO_2 that would have the same global warming effect for a given gas mixture. The gas mixture considered in this study for CO_2 equivalents consists of carbon dioxide, carbon monoxide, chloroform, nitrogen dioxide, ethane, methane and sulphur hexafluoride. The MJ primary energy needed is the energy needed to extract the same minerals in the future as were used presently.

2.3. Scale-up and Technology readiness levels

Scale-up, or scaling up, is defined in the Oxford Dictionary as: "Increase something (or be increased) in size or number". This definition is slightly limited and a more common explanation for it is: how to design a larger scale, pilot or industrial process or reactor that is able to replicate the results achieved in laboratory scale tests. Scaling up of chemical process and reactors is very

important and one of the main tasks for chemical engineers. It is a most important task in order to come to a fully functioning and optimized chemical plant, Donati and Paludetto (1997). Cumulated know-how from multiple phases of process development, from the design of the laboratory experiments, evaluation of kinetics and fluid dynamics, mathematical modelling as well as taking into consideration the design of both pilot and industrial scale plants is needed for a good scale-up of the process. There is no definite way of scaling up a process as each chemical process differs from the next. This can be because the kinetics are peculiar to a specific system. In many cases, the kinetics derived from lab-scale tests can be unimportant on a larger scale when transport phenomena and fluid dynamics start playing a larger role than in the perfectly mixed lab-scale reactors. Another reason why lab-scale results cannot be directly used for the design of larger scale systems is that industrial scale equipment very seldom functions in the same way as lab-scale equipment. One chemical reaction can be carried out in different types of reactors such as stirred tank reactors, fluidized bed reactors, distillation columns etc. and in different phases such as in a solution, suspension or even in a two phase system. Other things that will strongly affect the final design of the large scale setup are fouling, corrosion, impurities in the reagents as well as health, safety and environmental aspects (HSE).

Laboratory scale reactors should not be designed to replicate the conditions in the target-imagined process. The goal of the lab-scale tests is to study the reactions and give the best information possible. Key issues to study during the lab-scale tests in addition to kinetics are the fluid dynamics and the transport properties. All experiments should be carried out with the goal of scaling up the process in mind. The collected data should then be analysed using mathematical modelling and statistical tools. Based on these results some preliminary economic and process evaluations should be made in order to check if the process is (economically) feasible or not.

Building a pilot plant is usually very expensive and because of that the need for one has to be carefully evaluated. The main purpose of the pilot plant is to test the different technologies considered for the full industrial scale plant and to prove that the same results can be obtained in a larger scale compared to the lab-scale. This is important as some phenomena, such as reactions being limited by mass transfer rather than kinetics, might not be as evident in small scale tests as in large scale ones. In some cases, full pilot plants are not needed to evaluate and optimize the new process. Sometimes some tests can be carried out in

cheaper and more practical mock-up systems. Examples of such tests are heat exchange, flow patterns, residence times and mixing efficiencies.

Once an industrial scale plant has been built it should be monitored while data is recorded on how it functions. By analysing the collected data, both in real-time and offline, a better understanding of the process can be gained. The data can also be used to optimize and improve the already existing process. New control systems or procedures can be developed which can lead to increased yields or reduced consumption of raw materials, or reduced production of side-products and waste. The data can also be used later when developing similar processes.

One of the main hazards when scaling up a process is potential loss of control of an exothermic reaction. In case the full heat development is not fully understood and equipment is designed without keeping it in mind, catastrophic failures can occur. One of the reasons for this is the significant reduction in surface area of a reactor per unit volume with increasing size. The reduced area, in turn, gives a smaller heat exchange surface. For example a one litre cylindrical reactor with a surface area available for heat transfer of about 0.006 m^2 gives a surface area of 0.006 m^2/l, while a 1000 l reactor of the same shape has a surface area of 0.6 m^2 which gives a heat transfer surface area of only 0.0006 m^2/l. The available area per unit of volume is 10 times larger for the small scale reactor compared to that of the larger reactor. This can have significant impact on the temperature in the reactor and thereby also the yield and quality of the products. In case the feed of reagents is too fast and the temperature rises too fast, a thermal runaway can occur. This can, in the worst case, lead to an explosion which cannot only destroy the reactor but also cause harm to people nearby and to the environment. The risk of thermal runaway can be minimized if the lab-scale and pilot-scale tests are done thoroughly and sufficient heat exchange equipment is installed during the construction of the industrial scale plant.

The maturity of technologies is often measured using the Technology Readiness Level (TRL) measurement system originally developed by NASA (2008a, b). In this system, there are ten technology readiness levels with level zero being the lowest and level 9 being the highest. In some cases a level zero is also considered. A technology is at TRL-0 when it is still just an abstract idea with no scientific research to back it up. At TRL-1 one basic scientific research is started, while at TRL-2 the basic principals have been studied and practical applications have been formulated. Once a technology is being actively researched and the first designs are made a technology is elevated to TRL-3. At this stage, proof-of-concept models are made or constructed. During TRL-4

multiple component pieces or equipment are tested together, while at TRL-5 more rigorous testing is performed in environments that are as close to the final ones as possible. A technology reaches TRL-6 once a fully functional prototype or model has been achieved. To reach TRL-7 the prototype has to be tested and functional in the real environment for which the technology is intended. This can be seen as a pilot-scale plant test which should be over 5% of the final scale. To advance to TRL-8 a sub-scale demonstration plant (>25% of full scale) needs to be constructed and demonstrated. Once the technology is ready for full scale commercial implementation it can be considered to be at TRL-9. The technology readiness levels are summarized in Table 1.

Table 1 Technology readiness level summary

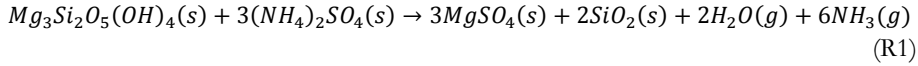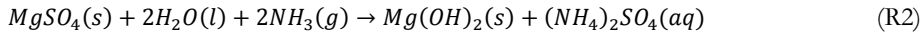| TRL-0	Idea
TRL-1	Basic principles observed and reported
TRL-2	Technology concept or application formulated
TRL-3	Analytical and experimental proof-of-concept
TRL-4	Laboratory component testing
TRL-5	Component prototype development
TRL-6	Component prototype demonstration (0.1-5% of full scale)
TRL-7	Pilot plant (>5% of full scale)
TRL-8	Sub-scale commercial demonstration plant (>25% full scale)
TRL-9	Full-scale commercial deployment

3. Processes
3.1. CCSM, ÅAU routes

Interest and research in carbon capture and utilization and storage (CCUS) by sequestration of CO_2 in mineral form (CCSM) has been driven by the too slow deployment of carbon capture and storage (CCS) technologies in general, and more specifically, by the high energy penalty of pre-separation of the CO_2 from flue gas together with the lack of suitable underground storage capacities in many locations, with Finland being one such location. One important advantage of the CCSM technology is the possibility of operating CO_2 mineralisation directly on a flue gas from a power plant or other CO_2 emitting source without an expensive CO_2 pre-separation ("enrichment") step with a high energy penalty. In addition to avoiding the a significant energy input penalty by using a CCSM technology, the problem of degradation the CO_2 capture solvent, such as amine solvent, due to the O_2 in the flue gas is also avoided.

One of the processes studied and optimized in this thesis is a process for mineral carbonation for long-term storage of CO_2. The process has been studied and developed at Åbo Akademi University, by Nduagu (2008, 2012a), Fagerlund and Zevenhoven (2011), Fagerlund (2012) and later by Romão et al. (2012a, b) and Romão (2015). The first ÅAU process involves carbonating magnesium hydroxide which is produced from serpentinite (magnesium silicate based) rock. In the first step of the process, serpentinite rock is reacted with ammonium sulphate at 400-440°C and atmospheric pressure. In the reaction sulphate salts of magnesium, calcium and iron are formed, as first described by Nduagu (2008) and Nduagu et al. (2012c, d). In addition to sulphate salts considerable amounts of ammonia, NH_3, water vapour and very small amounts of sulphur oxides, SO_2/SO_3, are released. Water is added to the solid reaction products in order to dissolve the water soluble sulphates. The insoluble fraction (mainly unreacted serpentinite and SiO_2) is discarded. NH_3 formed in the first step of the process is collected and later used to raise the pH of the aqueous solution, first to ~8-9 in order to precipitate out the dissolved iron and then to ~10-12 at which point the magnesium precipitates as magnesium hydroxide. The precipitated iron is in the form of (oxy-)hydroxides which can potentially be used as raw material in the steelmaking industry, Romão et al. (2012b), Koivisto (2013). This could potentially reduce the need for iron ore and thereby also reduce the emissions related to iron ore extraction. The precipitated $Mg(OH)_2$ is then fed to a pressurized fluidized bed reactor where it is carbonated at 500°C and 20 bar CO_2 partial pressure. The carbonation method is described in more detail by Fagerlund et al. (2011, 2012a). Not only pure CO_2 streams can be used for the carbonation but any gas stream, such as flue gas from a limekiln or blast
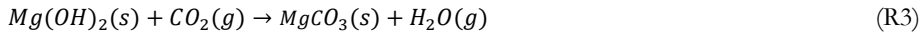
furnace, which contains a significant amount of CO_2 can be used as long as the partial pressure of CO_2 of the gas entering the carbonation reactor is 20 bar or above. For example for flue gas from a limekiln containing on average 20-21 vol-% CO_2 a total pressure of 80 bar would be needed. Ammonium sulphate salt is recovered from the left-over aqueous solution either through evaporation crystallization or with the use of mechanical vapour recompression (MVR). The main reactions for the mineral carbonation process are given below in Reactions 1 to 3

$$Mg_3Si_2O_5(OH)_4(s) + 3(NH_4)_2SO_4(s) \rightarrow 3MgSO_4(s) + 2SiO_2(s) + 2H_2O(g) + 6NH_3(g)$$

(R1)

ΔH=653.8 kJ/mol at T=440°C.

$$MgSO_4(s) + 2H_2O(l) + 2NH_3(g) \rightarrow Mg(OH)_2(s) + (NH_4)_2SO_4(aq)$$ (R2)

ΔH=-153.4 kJ/mol at T=30°C.

$$Mg(OH)_2(s) + CO_2(g) \rightarrow MgCO_3(s) + H_2O(g)$$ (R3)

ΔH=-22.96 kJ/mol at T=500°C.

Due to the conditions in the carbonation reactor all of the produced water exits the reactor as steam, leaving a dry solid product, as described by Fagerlund (2012). A schematic illustration of the process can be found in Figure 4 with a block diagram describing it in more detail in Figure 5.

The heat generated by the carbonation is ~ 1/3 of the heat that is needed for the magnesium extraction, making it necessary to use (waste) heat from, preferably, the process that generates the CO_2. In addition, compressing the entire flue gas requires a significant power input that to a large part can be recovered by expanding the "CO_2-free" vent gas.

Figure 4 A schematic illustration of the ÅAU CCSM process. [Paper III].

Several units and variables need to be studied in order to optimize the process. These are: the pre-treatment of the exhaust gas before compression, compression factors, compression stages, amount of cooling between each compression stage, pre-heating the gas before the reactor using the reactor outlet gas and recovery of exergy (see section 4.1) through the expansion of the gas after the reactor.

Figure 5 ÅAU CCSM process block diagram [Paper I] with ammonium sulphate (AS), solid/solid extraction (S/S extraction), heat exchanger (HX), precipitator (PP).

The ÅAU alternative process, presented in Figure 6, works in a similar fashion to the conventional ÅAU process except solid $Mg(OH)_2$ is not precipitated but instead the $MgSO_4$ containing solution is directly carbonated by addition of the NH_3 captured from the vapours of the first step, as for the conventional route,

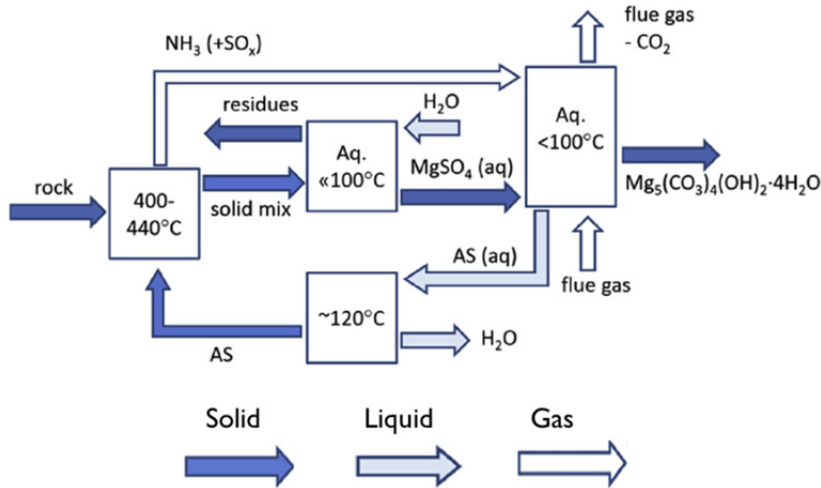while sparging with flue gas. The carbonation reaction takes place at ambient pressure and a low temperature ~ 30°C.

Figure 6 The alternative ÅAU route for CCSM [Paper III].
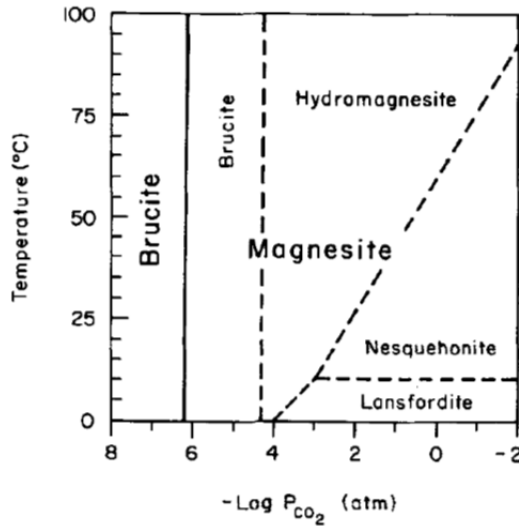
Figure 7 Phase diagram for MgO-CO_2-H_2O. Figure taken from Hill et al. 1982.

Depending on the temperature the magnesium products will primarily be nesquehonite ($MgCO_3 \cdot 3H_2O$) and hydromagnesite ($Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$). The conditions in the carbonation reactor are such that hydromagnesite is the most stable Mg-compound, as can be seen in Figure 7. This has also been confirmed by thermodynamic calculations using HSC 5.11 (see Paper IV) and

therefore, it is assumed that the reaction product will be hydromagnesite and the process chemistry is according to R1 followed by R4.

$$5MgSO_4 \ (s) + 10H_2O \ (l) + 10NH_3 \ (g) + 4CO_2 \ (g) \rightarrow$$

$$Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O \ (s) + 5(NH_4)_2SO_4 \ (aq) \qquad (R4)$$
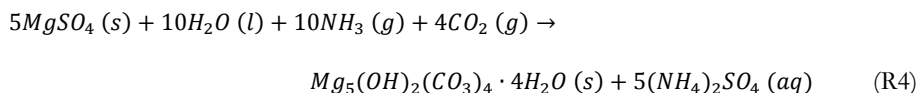
ΔH=-1082.2 kJ/mol at T=30°C.

The benefit of the alternative process is that it involves a simpler CO_2 contacting stage without the need for a pressurized fluidized bed reactor or gas compressors and expansion turbines. The downside of the alternative route is that no usable heat can be extracted from the low temperature carbonation reaction and the mass of product is higher with a lower CO_2 to Mg ratio. Also, water volumes for the carbonation step can be quite large.

3.2. Nanoparticles, BUONAPART-E process

Global demand for NP is increasing as new applications are invented. The increased demand for NP gives rise to the need for better and more efficient methods of production. For metallic NP, one such method could be the electric arc/spark discharge evaporation and condensation method studied in the EU Framework 7 Project BUONAPART-E (2012-2016), as has been summarized in the project final reports (BUONAPART-E 2016a, b).

The arc/spark-based method for metallic NP production has the potential of offering an alternative for other production routes, especially those that involve the use of complex chemicals that are difficult to recover for re-use. A relatively simple assessment of whether an alternative is economically viable and even preferable can be based on raw materials and waste handling costs and energy input requirements versus NP product market value. A deeper understanding that considers more factors, some related to upstream / downstream processes and others that address side-effects like pollution, losses during production and the impact of make-up chemicals, is obtained by LCA. Based on (database) data reported from existing processes, the LCI of production routes and products can be calculated, quantifying the environmental footprint.

As the knowledge of NP properties and the ways of utilizing the nanoparticles increase, the number of possible large-scale applications increases likewise. Due to this, ways to produce metallic NP at a larger scale and integrating the NPs into products have seen increased interest. Three nanometal products were identified and chosen for assessment of their environmental impact using LCA. The three products are NP zinc in polypropylene composite, copper NPs in

cooling water and silver NPs in textiles, respectively, - see Paper V. The product case studies were based on the life cycle models made for the production of the various metallic NPs presented earlier in Paper IV and expanded to include the NP integration into a product.
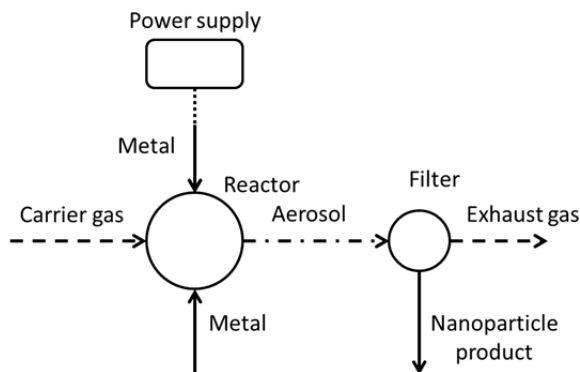

Figure 8 Basic function scheme for NP production unit [Paper IV]

A large amount data for NP production by electrical discharge evaporation has been produced by four project partners in the BUONAPART-E project. The data was collected from six equipment setups, with two types of discharges, arc and spark, at two different production scales for six metals (Ag, Al, Au, Cu, Ni, Zn) and two metal alloys (CuNi, FeCr). The collected data included the evaporation rate of metal, the collection rate of NPs on the product filter, carrier gas type, flow and consumption, specific electricity consumption (SEC) and NP product primary particle size. The work safety and risks involved were also studied during the project, (BUONAPART-E 2014).

The setups studied were low and high frequency spark discharge units, an arc discharge unit and multiple discharge units connected in parallel for low and high frequency sparks as well as for arc discharge. The groups at the University of Duisburg-Essen, Germany (UDE) and Metal Nanopowders Ltd., United Kingdom (MNL) operated systems based on arc discharge while Delft University of Technology, the Netherlands (TUD) operated both low and high frequency spark systems and Karlsruhe Institute of Technology, Germany (KIT-S) operated a low frequency spark system. Figure 8 shows the basic function scheme for an NP production unit consisting of an evaporation reactor, power supply and an NP collection filter.
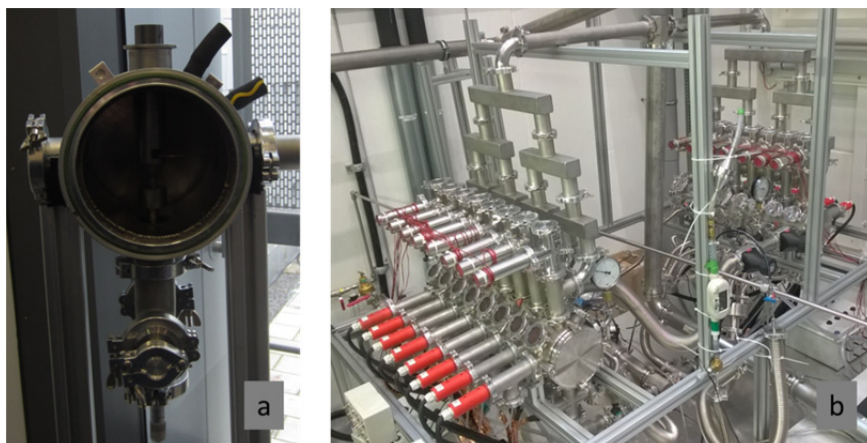
Figure 9 Pictures of evaporation units, a) single OSU and b) multiple (2x8) OSU both at UDE [Paper VI].

Several of the evaporation reactors can be built and connected in parallel in order to increase the production rate of NPs in a setup referred to as multiple OSUs (mOSU), (BUONAPART-E 2015a, b, c).

Figure 9 shows an arc OSU and an mOSU setup located at UDE. In Figure 9a, partly dismantled single OSU is shown while Figure 9b shows an mOSU setup consisting of two parallel reactor systems, each containing eight parallel OSUs. For the mOSU setup each OSU has its own power supply and metal pellet feeding system, while the gas feed and circulation system and NP collection filters are shared by all of the OSUs. For the OSU setup all of the supporting equipment, such as gas circulation pumps, NP filters and measuring equipment is dedicated to just the one evaporation unit.

The goal of the BUONAPART-E project was to develop the selected electrical arc/spark discharge evaporation and condensation technique to be able to produce several kilograms (up to 100kg) of nano-particles per day, BUONAPART-E (2015c). The work was divided into eight work packages (WP). Fundamental research into arc and spark discharge, plasma physics, modelling and *in-situ* measurements were part of WP1. WP2 focused on the optimization of the OSU while the development of supporting technologies, such as monitoring equipment, took place within WP3. The scale-up of the experimental facilities was done in WP4, while the process's suitability for production of NP for applications was studied within WP5. WP6 covered the LCA, HSE aspects and the techno-economic evaluation. Dissemination and project management was carried out within WP7 and WP8. ÅAU was mainly

part of WP6 (also as WP leader) with the tasks of evaluating the process in terms of energy efficiency and LCA as well as with the development of the process, process units and NP-containing products by the other partners. Most of this work was done by the author by evaluating the LCA of the arc and spark processes and by comparing the results with those for more traditional wet chemistry routes for producing similar metallic NPs.

The in-depth assessment was also done for three case studies that were considered to be the most advanced and well defined at this point within the BUONAPART-E project: use of copper NP as nanofluid dispersion in water for iron- and steelmaking cooling application, use of zinc NP co-extruded into poly propylene (PP) plastic as to enhance flame retarding properties, and use of silver NP in textile, giving it anti-bacterial properties.

4. Process evaluation

Both the CCSM process and the arc/spark NP production process have been evaluated using energy efficiency and exergy analysis, LCA and for scale-up. First both processes were evaluated using energy and exergy analysis in Section 4.1, then using LCA in Section 4.2 and finally on scale-up in Section 4.3.

4.1. Energy efficiency

Exergy analysis was chosen as the tool for optimizing the energy use and integration of the mineral carbonation process and the nanoparticle production processes. By doing an exergy analysis, which is based on the Second Law of Thermodynamics, it is possible to calculate the amount of useful work or maximum power that can be produced from any given energy form. The CCUS/CCSM processes were simulated in Aspen Plus® (v.7.2) by AspenTech (2015) and the obtained results were used to calculate the exergy for the streams using MS Excel®, while the exergies for nanoparticle production were calculated without any specific software.

Exergy analysis which is based on the Second Law of Thermodynamics allows for the calculation of the useful work or maximum power that can be produced from a given energy form (see e.g. Szargut et al. 1989). For a certain amount of heat, Q, at temperature T, with the surrounding temperature, T^0, the exergy can be calculated by:

$$Ex(Q) = Q \cdot \left(1 - \frac{T^0}{T}\right) \tag{2}$$

where the temperatures must be in K. This quantifies for how much useful work can be obtained by converting heat into power when taking the quality of the heat as given by its temperature into consideration when compared to the surrounding environment. For electricity, P, the exergy is equal to the energy:

$$Ex(P) = P \tag{3}$$

For given environmental conditions (here, $T° = 298.15$ K, $p° = 1.01325$ bar) the physical exergies E_{phys} of the compounds are calculated as function of temperature T and pressure p and standard physical exergy at T°, p°

where

$$Ex_{phys}(p, T) = \Delta H(p^0, T^0 \rightarrow p, T) - T^0 \cdot \Delta S(p^0, T^0 \rightarrow p, T) = (H - H^0) - T^0 \cdot (S - S^0)$$

$$\tag{4}$$

with enthalpy H, entropy S.

Chemical exergy for a compound or substance is given in reference to the reference environment, same as for physical exergy. The standard chemical exergy for a compound or a substance can be calculated using equation 5 from the chemical exergies of the elements, Ex^0_{chem}, and the standard Gibbs energy of formation, $\Delta_f G^0$.

$$Ex^0_{chem} = \Delta_f G^0 + \sum_{elements} n_{elements} \times E^0_{chem,elements} \tag{5}$$

(Szargut et al., 1989) where $n_{elements}$ is the number of moles of the element in a mole of compound and $E^0_{chem,elements}$ is the reference chemical exery of each element at ambient conditions.

For the assessment of the exergy destruction ΔEx_{loss}, also referred to as anergy, of a process or process unit, the sum of all exergy losses can be added up;

$$Ex_{losses} = \Delta Ex_{process} = -(\sum Ex_{out} - \sum Ex_{in}) = T^{\circ} \cdot \Delta S_{process} \tag{6}$$

4.1.1. Exergy analysis of CCSM routes

An envisioned pilot scale plant was modelled and simulated in order to evaluate the process and the exergy demand. It was originally designed to capture ~190 kg/h of CO_2 from 620 kg/h flue gas while processing 550 kg/h serpentinite at an industrial scale lime kiln. The model used – see Figure 5 – to simulate the process was made up of five main modules: solid/solid extraction module, dissolution and precipitation module, AS recovery module, carbonation with pre-heating and power production and finally the gas compression module. The material streams entering and exiting the process, with their mass flow, temperature, enthalpy, pressure and physical exergy, entering and exiting the modules are shown in Table 2. The original model for the simulation of this process was made by Romão et. al. (2012a), but in this work it was expanded in order to obtain more realistic results. Most of the work to improve the model was done for the utilization the flue gas heat together with the compression and utilization of the heat in the flue gas to be treated. By optimizing how the flue gas flows through each component in addition to the utilization of the heat of the hot flue gas exiting the carbonation process a significantly better heat optimization was possible compared to that reported earlier by Romão et al. (2012a), where pre-separated CO_2 was considered.

Most of the materials are assumed to enter the process at ambient conditions whereby their physical exergy is zero. In this work only the physical exergy of the chemicals and material streams are considered and shown in Table 2; the chemical exergy can be calculated by adding a value for the standard chemical exergy for the species to each stream, as mentioned above. Here, all exergy differences are calculated using eq (6), noting that $\Delta f G^0 = H_0 - T_0 S^0$. The exergy needed to drive the process comes from the hot flue gas and the electricity used to drive the compressors, the power needed to drive pumps and other equipment are assumed to be small compared to the overall exergy requirements and are not considered in this study. Even though the cooling water enters the process at ambient temperature, it has a small exergy due to it being pressurized. Table 2 also shows that most (~65 %) of the exergy that entered the process remains in the untreated flue gas as it leaves the process. This can be expected as the flue gas is still 384°C after it has been used to heat up the solid/solid extraction process. Other carriers of exergy are the medium hot water, recovered AS and the solid magnesium carbonate product. The expansion turbines used to recover power are another significant source of exergy. The exergy demand for the crushing and grinding of the serpentinite is omitted as the exergy requirement is very low compared to the overall process, as reported by Romão et al. (2012a) and later confirmed by Yuen et al. (2016).

Optimizing the flue gas compression train is very important, as the compression system is the largest exergy consumer after the magnesium extraction from the mineral step according to Romão et al. (2012b). Exergy analysis was used to optimize the compression system. In order to minimize the exergy loss in the compression system several units and variables have to be considered, among these are: the pre-treatment of the flue gas before compression, compression factors, number of compression stages, amount of cooling between each compression stage, pre-heating of the gas before the carbonation reactor using the reactor outlet gas and recovery of exergy through the expansion of the gas after the reactor using expansion turbines. The compression train was simulated using three, four or five compression stages. Using five compression stages instead of three reduces the exergy demand by close to 10% with the optimal compression strategy of having constant compression ratios in the first four compression stages and a higher compression rate in the last stage -see Paper II. The benefit of having a higher compression stage in the last stage is that a higher outlet temperature is achieved which, in turn, requires less heat to reach the required temperature in the carbonation reactor. The energy demand of the compression system is between 1.225-1.675 GJ/ton CO_2 compressed. In order to minimize the overall energy cost of the compression system efficient

equipment for both the compression and expansion is needed coupled with an efficient carbonation reactor with a high CO_2 conversion rate.

Table 2 Overall simulated material and energy streams of ÅAU CCSM process [Paper I].

Total process	Mass flow kg/h	Temperature °C	Enthalpy flow (total) kW	Pressure bar	Exergy (physical) kW
In					
Ammonium sulphate	1100	15	-2267.3	1	0
Serpentinite (from Hitura mine)	550	15	-2166.8	1	0
Flue gas in (used only as heat source)	28000	500	-20826	1	1730.0
Dissolution water	900	15	-3976.8	1	0
Cooling water for solids	90	15	-397.68	1	0
NH_3	0.1	15	-0.076	1	0
Flue gas	620	500	-461.14	1	38.3
Cooling water	800	15	-3534.9	4	0.042
Compressors					118.1
Exergy in (heat in material streams)					**1768.3**
Exergy in (power)					**118.1**
Out					
Flue gas out	28000	384	-21849	1	1120.0
Hot water from solids cooling	90	100	-386.0	1	1.7
Undissolved solids	298	80	-1120.0	1	50.0
Precipitate I	36	30	-64.8	1	16.1
Evaporated water	523	100	-2023.1	1	60.4
Medium hot water	800	100	-2952.3	1	124.4
Recovered AS	1441	103	-4682.3	1	128.0
Solid product ($MgCO_3$)	386	150	-1421.3	1	127.8
CO_2-lean gas	489	92	-289.2	1	5.4

Condensate	21	41	-91.7	1	0.026
Turbines					72.2
Exergy out (heat in material streams)					**1633.6**
Exergy out (power)					**72.2**
ΔEx heat					**134.8**
ΔEx power					**46.0**

The amount of hot flue gas needed to cover the heating demand for the CCS process can be significantly reduced by optimizing the heat exchanger network and by utilizing waste heat generated inside the CO_2 mineralization process. Compared to results published earlier by Romão et al. (2012a), the need for hot flue gas for pre-heating can be reduced by 32 %, from 42434 kg/h to 28620 kg/h flue gas. Thanks to this it would be possible to increase the scale of the envisioned pilot plant based on the available heat from fixing ~190 kg/h to ~260 kg/h CO_2 with the same heat input and using 550 kg/h serpentinite.

Finally it is possible to calculate the overall exergy demand per ton CO_2 sequestered for heat and power to be 485 MJ and 166 MJ, respectively (equivalent to 9 kg CO_2/h using the national emission average value for Finland of 200 g CO_2 per kWh [Paper II]), processing 550 kg rock/h and sequestering 187 kg CO_2/h, which gives a net sequestration of 178 kg CO_2/h, which is ~1400 t CO_2/year. For the alternative ÅAU route the overall exergy demand is 2930 MJ heat to sequester the same amount of CO_2 – see Paper III.

4.1.2. Exergy and energy analysis of nanoparticle production by discharge evaporation

The energy requirement for producing metallic NP has been measured by four project partners within the BUONAPART-E project group. The measurements were carried out by UDE, MNL, TUD and KIT-S for all the metals studied. Due to only a few tests carried out with most metals and a few alloys, here the three metals with the most data available have been focused on. These metals are silver, copper and zinc. These are also the metals that were identified as the ones with the greatest market potential within the project. The collected and summarized data for the three metals mentioned is shown in Table 3.

The production rate given in Table 3 is the amount of metal evaporated, while the collected mass is the total mass of the NP that is collected on the particle filters and can be obtained as product. The specific electricity consumption (SEC) is the amount of electricity used to evaporate the metal divided on the mass of product particles or the total surface area of the particles. For copper NP produced with a single OSU with an arc discharge the SEC varies from 0.13 kWh/g to 0.25 kWh/g for particle sizes 74 nm to 45 nm. The electricity consumption goes up significantly as the product particles become smaller.

Most BUONAPART-E partners interpreted energy use, SEC, as the "energy efficiency" of the process, but in order to evaluate the efficiency of the process obviously a thermodynamic minimum energy needs to be calculated. This can then be compared to the experimental data using exergy analysis. Evaluating the nanoparticle production process by means of exergy cannot be done in the same way as for the CCSM process. In this process the main change of the feedstock to product is the change in surface area. The material is transformed from a bulk material into NPs with a much larger total surface area per mass. For this reason the exergy needs to be calculated in another way, as recently reported by Zevenhoven and Beyene (2014) and summarised here.

Table 3 Summary of NP production data: silver, copper, zinc. [Paper VI]

	Partner	Carrier gas	Production rate	Collected mass	Collection efficiency	Power use	SEC	SEC	Primary particle size
			g/h	g/h	%	kWh	kWh/g	kWh/m²	nm
Silver									
OSU spark	TUD	Ar	0.09	0.072	80	0.036	0.500	0.037	5
mOSU HF spark	TUD	N₂	1.2	0.96	80	1.5	1.56	0.23	10
OSU arc	UDE	N₂	1.6-7.2	0.2-1.0	13.9-31.3	0.29-0.96	0.57-0.96	1.05-1.64	115-128
	MNL		13.9	2.6	18.7	1.6	0.62	0.14	15.7
Copper									
OSU spark	TUD	Ar	0.03	0.024	80	0.036	1.50	0.112	5
	KIT-S	N₂	0.0009	0.000405	45	0.020	49.3	3.157	4.3
mOSU HF spark	TUD	N₂	1.3	1.04	80	1.5	1.44	0.21	10
OSU arc	UDE	N₂	6.2-20.2	1.3-5.7	21-33	0.33-1.02	0.13-0.25	0.14-0.20	45-74
	MNL		71	13.5	19	1.88	0.14	0.12	58
mOSU arc	UDE	N₂	272.16	68.04	25	10.5	0.154	0.181	79
Zinc									
OSU spark	TUD	Ar	0.09	0.072	0.036	0.5	6.944	0.516	5
	KIT-S								
OSU arc	UDE	N₂	6.6-42	4.9-21	50-74.2	0.11-0.3	0.014-0.022	0.05-0.057	150-270
	MNL	Ar	27.8	5.3	19.1	0.4	0.075	0.165	147

For the increased surface energy for atoms of NP material, literature data for surface free energy (SFE) γ can be used, given typically as a linear function of temperature T, and (bulk) melting temperature T_{mb}, with two material parameters $\gamma(T_{mb})$ and b:

$$\gamma(T) = \gamma(T_{mb}) - b \cdot (T_{mb} - T) = \gamma(0\,K) + b \cdot T, \quad J/m^2 \quad with \quad b = \frac{d\gamma}{dT}, \tag{7}$$

Here the creation of surface A = $6/(\varrho \cdot D)$, m² per unit mass for spherical NP with diameter D and density ϱ requires work W, i.e. exergy quantified by the SFE equals to

$$Ex_{surf}(D,T) = A \cdot \gamma(D,T) \cdot (1 - \frac{P}{D}) \qquad J/kg \tag{8}$$

where P is the power/electricity fed to the system to create the surface area and the last term (1 – P/D) accounts for the finding that SFE decreases with diameter for small NPs, especially for NPs smaller than 50 nm, as elaborated by Xiong et al. (2011). They also show how temperatures of melting and evaporation, T_m and T_v, as well as the enthalpies for this, ΔH_m and ΔH_v are lowered for small NPs compared to bulk material properties:

$$\frac{T_{m,NP}}{T_{mb}} = (1 - \frac{P}{D}) = \frac{T_{v,NP}}{T_{vb}} \quad where \quad P = -\frac{\pi \cdot N_{Avogadro} \cdot d^3 \cdot b}{\Delta S_{mb}} = -\frac{\pi \cdot N_{Avogadro} \cdot d^3 \cdot b \cdot T_{mb}}{\Delta H_{mb}}$$

$$\Delta H_{m,NP} = \Delta H_{mb}\left[1 - \left(1 + \frac{3R}{2\Delta S_{mb}}\right) \cdot \frac{P}{D}\right] \quad and \quad \Delta H_{v,NP} = \Delta H_{vb}\left[1 - \left(1 + \frac{3R}{2\Delta S_{vb}}\right) \cdot \frac{P}{D}\right] \tag{9}$$

defining parameter P, with diameter d for one atom (~0.3 nm for the metals considered).

The fact that temperatures for melting/solidification and evaporation/condensation depend on NP size results in a second energy penalty for the thermal NP production method using arc/spark discharges. Energy that is needed as heat for melting and evaporation of (bulk) metal is later released as heat of condensation and solidification of NP material, however for both processes at a lower temperature, as discussed by Zevenhoven and Beyene (2014). For the melting and solidification this gives an overall energy input requirement as electricity equal to an exergy difference quantified by:

$$Ex_{Q,melt/solidify} = \Delta H_{mb} \cdot \left(1 - \frac{T^\circ}{T_{mb}}\right) - \Delta H_{m,NP} \cdot \left(1 - \frac{T^\circ}{T_{m,NP}}\right) \tag{10}$$

$$Ex_{Q,melt/solidify} = Ex_{Q,melt} - Ex_{Q,solidify}$$

and a similar expression for the overall energy effect of evaporation and condensation.

With the help of these equations the electrical energy input requirements for copper NP can be calculated, for example, (γ (T_{mb}) = 1.576 J/m^2, b = -0.338 mJ/m^2·K, d = 0.283 nm, P = 1.497 nm, T$^\circ$ = 298 K) giving the results as given in Figure 10, for five different NP sizes.
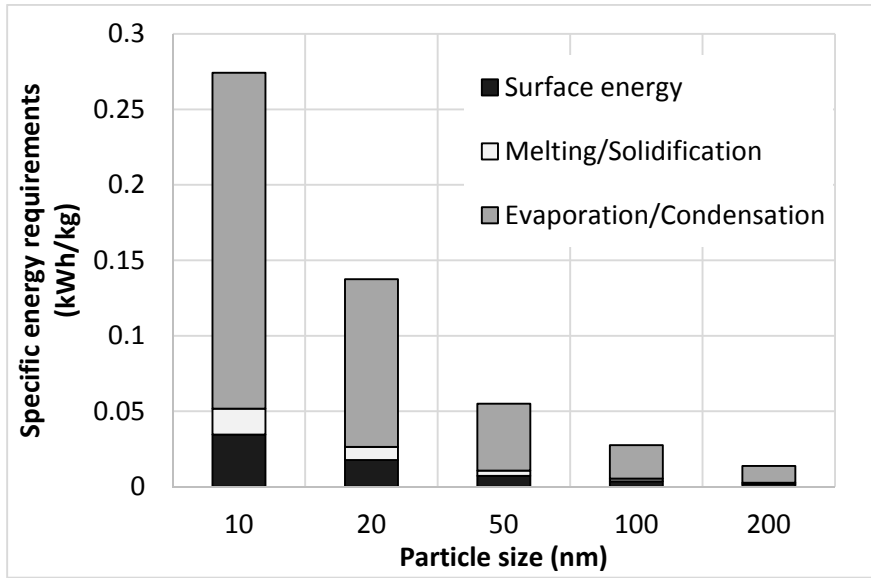

Figure 10 Theoretical minimum electricity input requirements for producing copper NP. [Paper VI]

As can be seen in Figure 10, the thermal effects of this route give a much larger contribution to the energy input requirements than the creation of surface energy does.

Comparing the minimum energy input required calculated by exergy analysis to the experimental results shows that the calculated value is several orders of magnitude lower than experimental values. For copper NP of ~ 50 nm the measured SEC was ~ 250 kWh/kg, while the calculated minimum is 0.06 kWh/kg. The same difference was found for other metals.

Part of the large difference between the measured SEC and the thermodynamic minimum can be explained by the power loss in the AC/DC converters used for powering the arc (10% of the energy is lost as heat) and the low capture rate of the product which at times was as low as 20%. This leads to a factor of five increase of the SEC, as there is less product mass to account the input energy to. By improving the flow of particles in the setup and thereby reducing the material loss the SEC can be significantly reduced. Other sources of energy loss are the loss of energy to the cooling system as well as conductive and heat radiation losses; these make up for 17-34% and 24%, respectively, based on a series of tests at UDE by ÅAU using a thermal camera and several other devices. Taking these factors into account the SEC for 50 nm copper NP would be ~ 22.5 kWh/kg.

The primary way of reporting the SEC for the electrical discharge evaporation and condensation process for producing the NPs was evaluated based on the mass of particles. This can be somewhat misleading as NPs of different size can have different properties, such as total surface area per unit of mass. Therefore, the electricity demand for producing NPs was also compared considering the produced primary particle surface area.

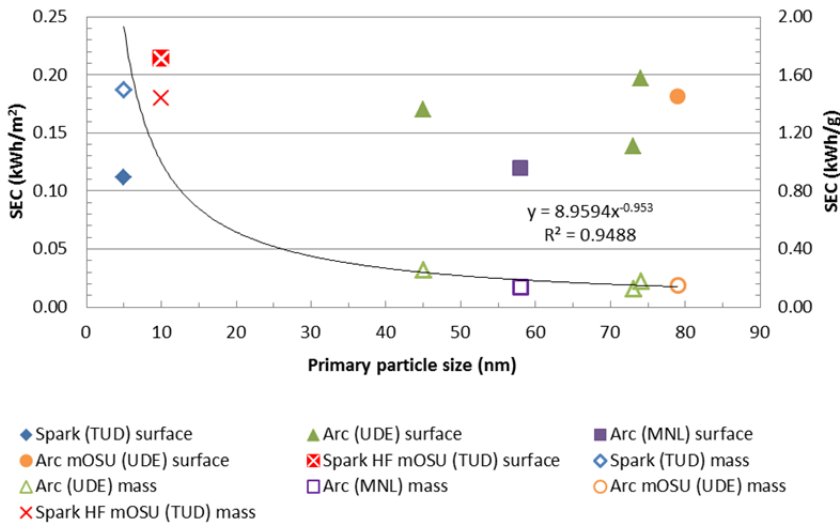$$y = 8.9594x^{-0.953}$$
$$R^2 = 0.9488$$

Figure 11 Specific electricity consumption for NP production, filled points: surface area, open points: mass. Figure taken from Paper V.

Figure 11 shows the SEC for producing copper NPs of varying primary particle size with different methods and setups. As can be seen, there is no clear correlation between the SEC per surface area and the primary particle size, the

best fit of the data only gives an regression coefficient, R^2, of only 0.02. When looking at the SEC as a function of produced mass it can be seen that the SEC per mass is similar for 45 to 80 nm NPs, while the SEC for the 5 nm particles was significantly higher. This can be explained by the exergy analysis given above. There seems to be a clear correlation in the SEC needed to produce one gram of specified particle size NPs, as can be seen by the trend line in the figure. The curve fitted to the measured data has a good correlation with the R^2 being 0.95. Based on this finding calculating the SEC as a function of mass has merit from the point of view of the energy efficiency of producing the NPs.

4.2. Life Cycle Assessment
4.2.1. Life Cycle Assessment of CCSM routes

The LCA study of the ÅAU CCSM processes, both with dry carbonation and wet carbonation options, were performed as cradle-to-gate studies with the functional unit the capture of one kilogram CO_2. In order to capture/sequester one kilogram of CO_2 it is necessary to produce 2.03 kg $MgCO_3$ or 2.65 kg $Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$, respectively. When comparing these values to the ones reported in Paper III, it is apparent that they differ for the wet carbonation route. In Paper III, the carbonation processes were calculated with more realistic variables for the wet route, based on experiments, while the values reported here are based on 100 % conversion of Mg to $Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$ which would require the production of 505 kg $Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$ in order to capture 190 kg of CO_2 unlike the 353 kg product reported in Paper III. The mining of the serpentinite used for the $Mg(OH)_2$ or $MgSO_4$ production, production and recycling of ammonium sulphate, production of process water, generation of electricity used in the process and the shipping of the serpentinite and ammonium sulphate as well as the production and shipping of ammonia were included in this study. The serpentinite is assumed to be mined at the Hitura nickel mine and shipped to a CCSM plant at an industrial lime kiln in Parainen, Finland, (550 km) by truck, 99.5 % of the ammonium sulphate is recycled within the process and fresh ammonium sulphate and ammonia are transported to the site by truck (200 km) from a regional storage facility. Generation of electricity used in the process is assumed to be the same as for the average grid mix in Finland, Ecoinvent (2012). The impact of infrastructure was not considered, neither was the end-of-life phase of the product. Figure 12a shows the system boundary for the dry carbonation process and Figure 12b shows the boundary of the wet carbonation process. The flue gas comes from a lime kiln which is also outside the boundary of the study. The heat used in the extraction stage of the process is taken from the waste heat generated at the lime kiln.
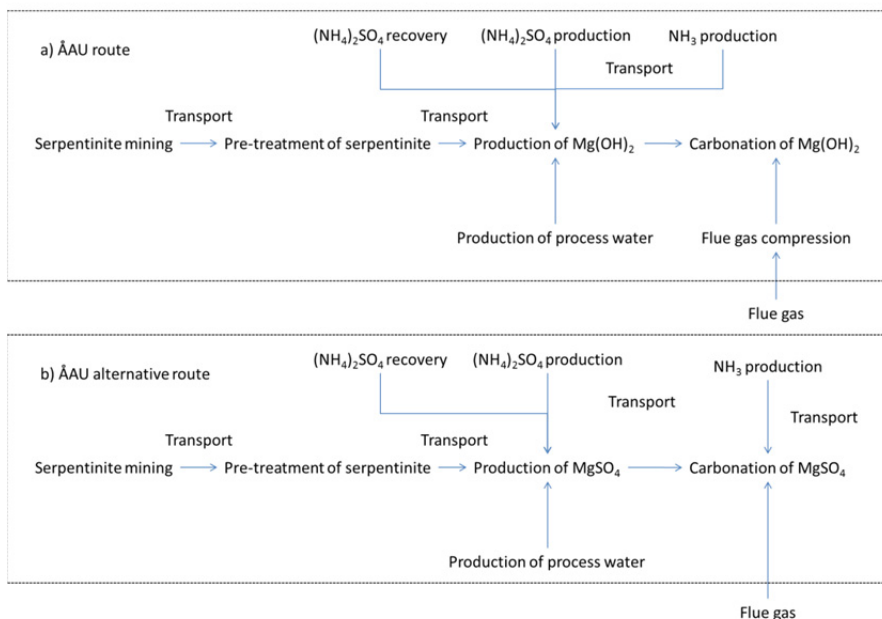
Figure 12 LCA system boundaries for the ÅAU conventional, a), and alternative, b), routes for CCSM case-studies

As can be seen in Figure 13 and Table 4, the total process is GHG negative for the dry carbonation route. Per one kilogram of CO_2 sequestered the net amount of reduced CO_2 emissions is 0.445 kg CO_2 which corresponds to ~44.5 %. The main cause of GHG emissions from the CCSM process comes from the compression of the flue gas to the required 80 bar(g) for fast carbonation of the $Mg(OH)_2$ (minus the expansion of the "CO_2 free" flue gas) and the transport of the serpentinite rock from the mine to the carbonation plant.
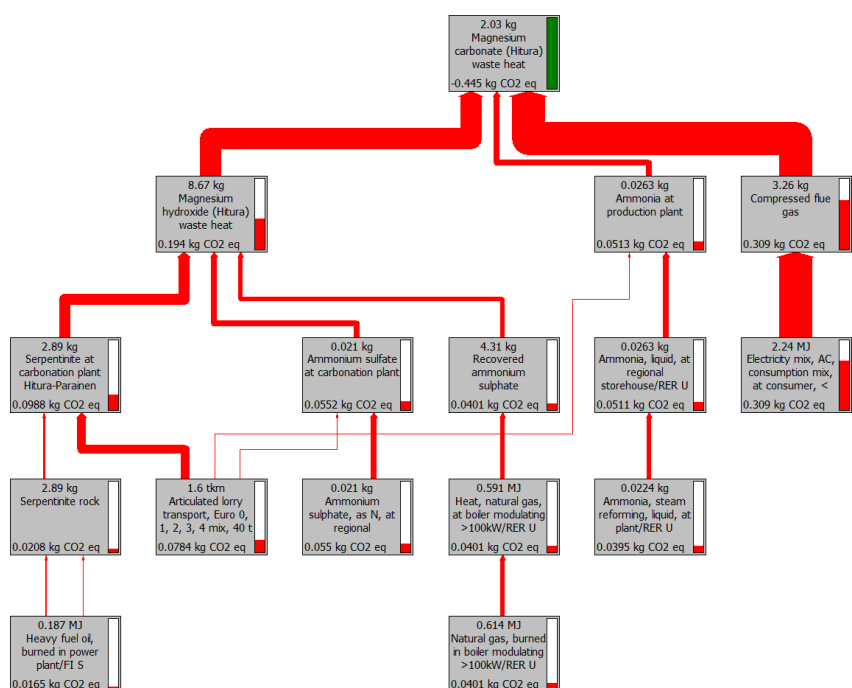
Figure 13 LCA network showing the GHG emission for the nodes with the largest impact for the ÅAU route for CCSM process

Even though the emissions of GHGs are negative for the process, there are other impacts on the environment that need to be considered. The process has a negative effect on the environment in the Human health (2.4·10⁻⁰⁷ DALY), Ecosystem quality (0.0211 PAF m² yr) and Resource depletion (9.24 MJ Primary energy) categories. Whether this environmental impact is acceptable is a subject which will not be discussed in this thesis.

Table 4 Environmental impact for ÅAU CCSM process for capture of CO_2 from a lime kiln per one kg of sequestered CO_2.

	Human health	Ecosystem quality	Climate change	Resource depletion
	DALY	PAF m² yr	kg CO_2 eq	MJ Primary
Carbonation	0	0	-0.999	0
MgOH	$1.18·10^{-7}$	0.014	0.194	3.16
AS	$2.18·10^{-7}$	0.002	0.051	1.09
Compressed flue gas	$1.00·10^{-7}$	0.005	0.309	4.98
Total process	$2.40·10^{-7}$	0.021	-0.444	9.24

Ammonium sulphate (AS)

For the ÅAU alternative route for CCSM it can be seen in Figure 14 and Table 4 that the majority of the CO_2 equivalent emissions come from the transport of the serpentinite rock. The transportation also stands for the biggest impact in the Human health category, while the production and transport of the fresh ammonium sulphate is the largest contributor to the impact in the Ecosystem quality category and the recovery of ammonium sulphate contributes the most in the Resource depletion category. The net effect of sequestering one kilogram of CO_2 with the wet carbonation route is a CO_2 emissions reduction of 0.74 kg CO_2 which corresponds to 74 %.
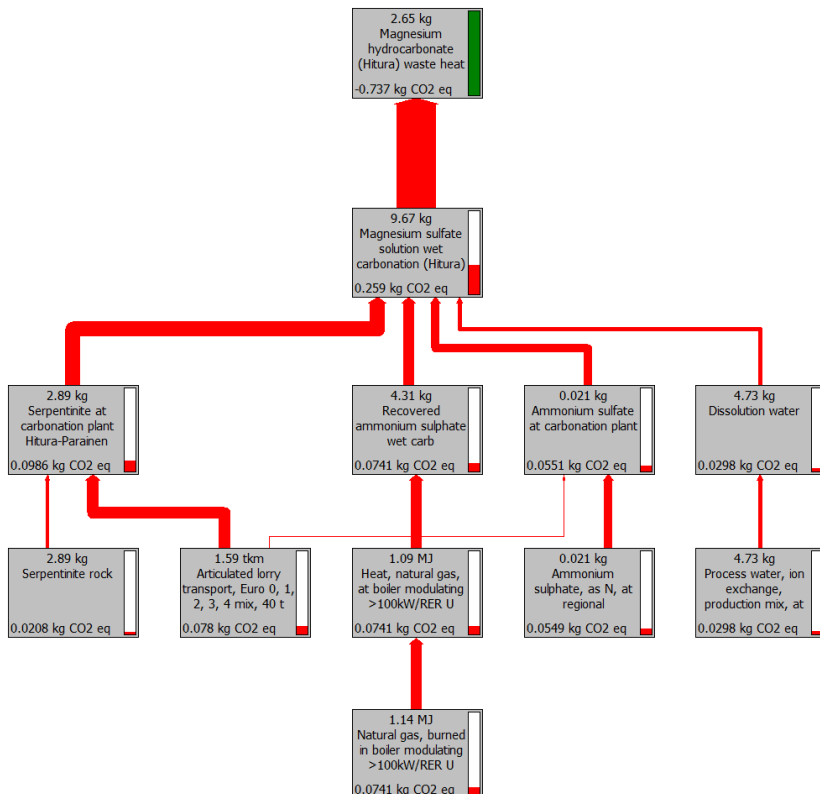

Figure 14 LCA network showing the GHG emission for the nodes with the largest impact for the ÅAU route for CCSM process

The total emissions for the ÅAU alternative route for CCSM are $1.31 \cdot 10^{-07}$ DALY, 0.014 0.0211 PAF m² yr, -0.74 kg CO_2 eq and 4.24 MJ Primary energy in the Human health, Ecosystem quality, Climate change and Resource depletion categories.

Table 5 Environmental impact for ÅAU alternative route for CCSM process for capture of CO_2 from a lime kiln per one kg of sequestered CO_2

	Human health	Ecosystem quality	Climate change	Resource depletion
	DALY	PAF m^2 yr	kg CO_2 eq	MJ Primary
Serpentinite rock				
Mined	$2.26\cdot10^{-8}$	0.0027	0.02	0.31
Transport	$6.52\cdot10^{-8}$	0.0037	0.08	1.12
AS				
Recovered	$7.49\cdot10^{-9}$	0.0003	0.07	1.41
Fresh	$2.63\cdot10^{-8}$	0.0070	0.06	0.97
Dissolution water	$9.08\cdot10^{-9}$	0.0005	0.03	0.40
Fresh ammonia	$7.40\cdot10^{-10}$	0.0001	0.00	0.04
Carbonation	0	0	-1.00	0
Total process	$1.31\cdot10^{-7}$	0.014	-0.74	4.24

Ammonium sulphate (AS)

When comparing the dry carbonation route with the wet carbonation route, see Table 4 and Table 5 respectively, it is clear that the wet carbonation route has a much smaller environmental footprint. In both the Human health and Ecosystem quality categories the environmental impact of the wet carbonation route is almost half of that for the dry carbonation route. The CO_2 reduction in the Climate change category is almost double for the wet route compared to the dry carbonation route, while in the Resource depletion category the impact is only ~40 % for the wet route compared to the dry.

In case the serpentinite could be brought from either Vammala or Parainen instead of Hitura the distances the mineral would need to be transported would be significantly shorter. The distance from Vammala to Parainen is around 150 km, while the mineral in Parainen would only need to be transported a few kilometres to the CCSM plant. The effect of transport distance on the overall LCI of the CCSM process (dry carbonation) is given in Table 6. As can be seen, this effect is small.

Table 6 Effects of transportation distance of the magnesium containing mineral on overall process environmental impact for dry carbonation utilizing waste heat

	Human health	Ecosystem quality	Climate change	Resource depletion
	DALY	PAF m^2 yr	kg CO_2 eq	MJ Primary
Hitura-Parainen (550 km)	$2.40 \cdot 10^{-7}$	0.021	-0.445	9.24
Vammala-Parainen (150 km)	$1.93 \cdot 10^{-7}$	0.018	-0.501	8.43
Parainen-Parainen (5 km)	$1.78 \cdot 10^{-7}$	0.017	-0.5189	8.17

4.2.2. Life Cycle Assessment of nanoparticle production process

The LCA study carried out for the production of NPs by arc or spark discharge evaporation is a cradle-to-gate study which takes into account the impact of the mining, refining of the metals, production of carrier gas through separation from air, and the transport of both gas and metals to the NP production plant. Generation of electricity used to evaporate the metals in the NP production process was also taken into account, power generation was assumed to be according to the low-voltage grid mix of either Germany or Spain. Both German and Spanish grid mixes were used, as both countries were seen as likely locations for the NP production facilities. The environmental impact caused by infrastructure was not considered.

Figure 15 shows the system boundary for the studied process (here for a Zn in PP nanocomposite). The system boundary presented in the left box of Figure 15 was used for the production of the metallic NPs discussed in Section 3. In order to study the NP containing products the system boundary was expanded in order to take into account the further processing of the nanoparticles after synthesis, the production of the other components of the product and the integration of the nanoparticles. For the NP-containing products the system boundary encompasses both the left and right boxes.
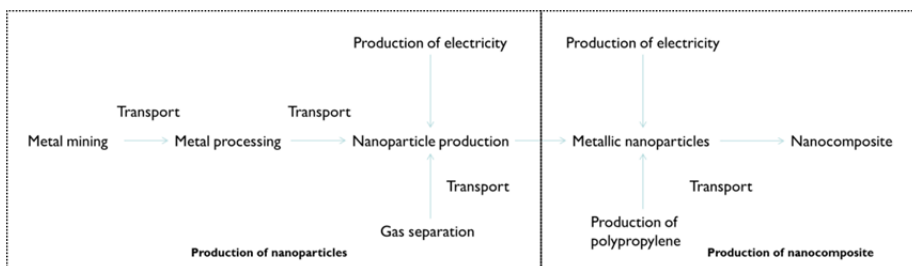
Figure 15 Schematic representation of the system boundary for zinc in polypropylene case study

In order to evaluate the environmental impact of the electrical discharge method it needs to be compared to other methods for nano-particle production. The studied method is a non-chemical route for producing the particles and chemical synthesis routes were selected for comparison.

The functional unit for the life cycle impact studies was the production of one kilogram NPs or one kilogram of NP-containing product. In the study, the mining and refining of metals used for NP production, production of carrier gas and electricity used in the process and the shipping of the metals and gases were included, while product use and end-of-life product handling are not considered.

Pure metallic nanoparticles

For the electrical discharge evaporation process, the model used for the calculation of the life cycle impact for analysed metals is very similar. An ultra-pure wire of the specific metal is connected as the anode and is evaporated by electric discharges. Pure nitrogen or argon gas is used as carrier gas. The process is modelled starting from metal at a primary metal producing plant, nitrogen or argon gas is produced through cryogenic air separation and electricity is produced in Germany with an average mix of power production technologies according to Ecoinvent 2.2. The pure metal is shipped (15000 km assumed here by container ship from Australia) to the NP production plant where it is treated in order to obtain the required purity before being shaped to the wire used as the anode. The carrier gas is produced close to the NP production plant and shipped in gas bottles by trucks (20 km) and a recovery/recycle rate of 99.5 % was assumed based on experiments at UDE. During the comparison of the dry evaporation route with the wet chemical routes, the recycling of materials such as carrier gas and material stuck inside the reactor housing and tubing was not considered.

For the wet chemical routes the production of the reagents and the transport of these to the NP production facility as well as the energy needed to produce the NPs were taken into account. The environmental impact of the particles after production was not considered. A major reason for this is that data on this is simply not available. The required size and shape, as well as what metal is being used, determine the synthesis route and therefore there are no standard chemical routes for producing metallic NPs. Only NP production methods with sufficient data on the synthesis route published and using chemicals or precursors available in the Ecoinvent 2.2 database or that can be modelled with the base chemicals available in said database, were considered and used. As most of the data available was for chemical reduction of a metal containing precursor, this was selected as the synthesis route for Ag, Cu and Zn. The synthesis routes are similar for both copper and silver, with the same reducing agent being used, while the synthesis of zinc NPs is significantly different with the main difference being the use of another reducing agent. The final yields of the NP product by conventional wet production routes were poorly reported for Ag, Cu and Zn and, therefore, similar yields as for the arc/spark process were assumed.

The absolute values for the different impact categories are not the main focus in this study; emphasis is placed on the comparison of the different methods. Even though the actual material yield of the arc/spark setups are low, around 20% as shown in Table 3, the environmental impact was evaluated for the best case scenario of a product yield of 100% in order to compare it to the unreported yield of the wet chemical routes which was also assumed to have a 100% material yield. As can be seen in Table 7, the biggest impact on Human health and Ecosystem quality comes from the pure copper used for the process, while the electricity used is the main cause of Climate change and Resource depletion. The impact of the nitrogen gas can easily be reduced by recirculating the gas after it passes through the particle filter.

Table 7 Environmental impact for arc method of producing copper nanoparticles at 100% yield. [Paper V]

	Human health	Ecosystem quality	Climate change	Resource depletion
	DALY	PAF m^2 yr	kg CO_2 eq	MJ Primary
Nitrogen gas	0.000001	0.05	1.96	37.33
Pure copper	0.000061	40.39	4.97	93.18
Electricity	0.000003	0.19	18.15	292.70
Total	0.000065	40.63	25.08	423.21

The environmental impact for the wet chemical route for production of Cu NP was divided into two, the copper containing precursor and the reducing agent, respectively. As can be seen in Table 8, the production of the copper precursor is the main cause of Human health and Ecosystems quality impacts. The high environmental impact of the sodium borohydride used as the reducing agent leads to the production of the reducing agent having the largest impact on the Climate change and Resource depletion categories.

Table 8 Environmental impact for chemical reduction method of producing copper nanoparticles at 100 % yield. [Paper V]

	Human health	Ecosystem quality	Climate change	Resource depletion
	DALY	PAF m² yr	kg CO_2 eq	MJ Primary
Copper precursor	0.00009	36.92	20.45	266.34
Reducing agent	0.00004	11.93	64.78	997.42
Total	0.00013	48.85	85.23	1263.76

The results of the life cycle impact assessment for both the dry route and the wet route are compared in Figure 16. It shows how the choice of production method for Cu NP affects the impact in the Human health, Ecosystem quality, Climate change and Resources categories. In addition to showing the results for 100% material yield, the measured yield for the dry route is also shown. In all four impact categories the dry method has a lower impact than for the chemical reduction method, for similar production yields. It is only in the Ecosystem quality category where the impacts of the evaporation and chemical route are similar. For similar evaluations for Ag, Zn and Al, see Paper IV.
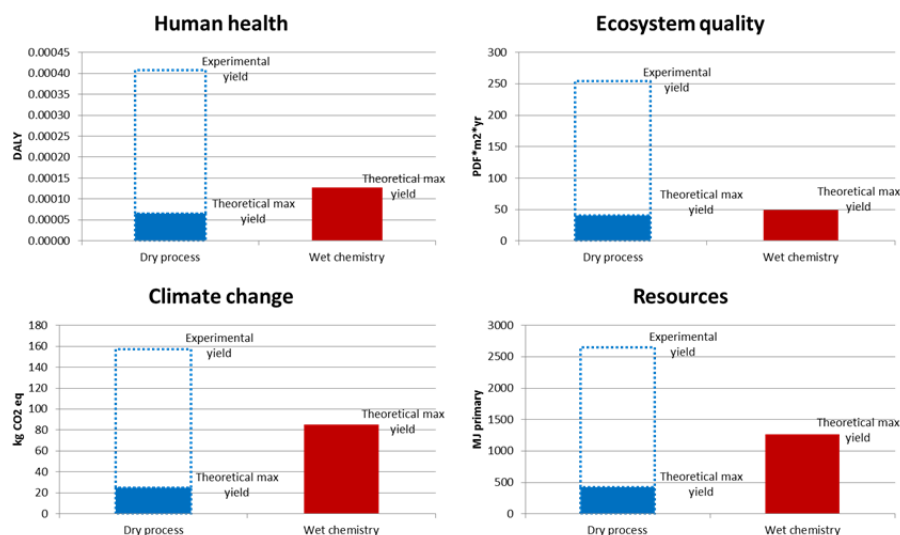
Figure 16 Life cycle impact comparison for evaporation method and chemical reduction method for copper particles. [Paper IV]. The theoretical max yield is assumed to be 100% while the experimental yield was 20%.

Nanoparticle containing products

Textiles are coated with nanoparticles in order to give anti-bacterial properties to textiles used in medical clothing and bedding produced by Spanish project partner *Fundación para el fomento del sector textil de la Comunidad Valenciana*, Spain (FOMENTEX). The antibacterial effects of nanoparticles have been studied in great detail by Hajipour et al. (2012). For the study of the life cycle impact of silver treated textile it is assumed that the particles are produced on-site at the textile treatment plant in a similar fashion as described above for Cu NPs with exception of using electricity produced as that from the Spanish grid mix. The textile material, cotton, as well as acrylic and polyurethane resins are transported to the plant by truck; here the transport distance is assumed to be 500 km. Silver nanoparticles are mixed with either an acrylic or polyurethane resin in order to create a paste that is used to treat the textile. Once treated with the NP containing resin the textile is dried using heat supplied by a natural gas burner. The environmental impact of the cotton and resins are according to the data available in the Ecoinvent 2.2 database. Here the goal was to compare the different sources of environmental impact of the production of the NP treated textile.
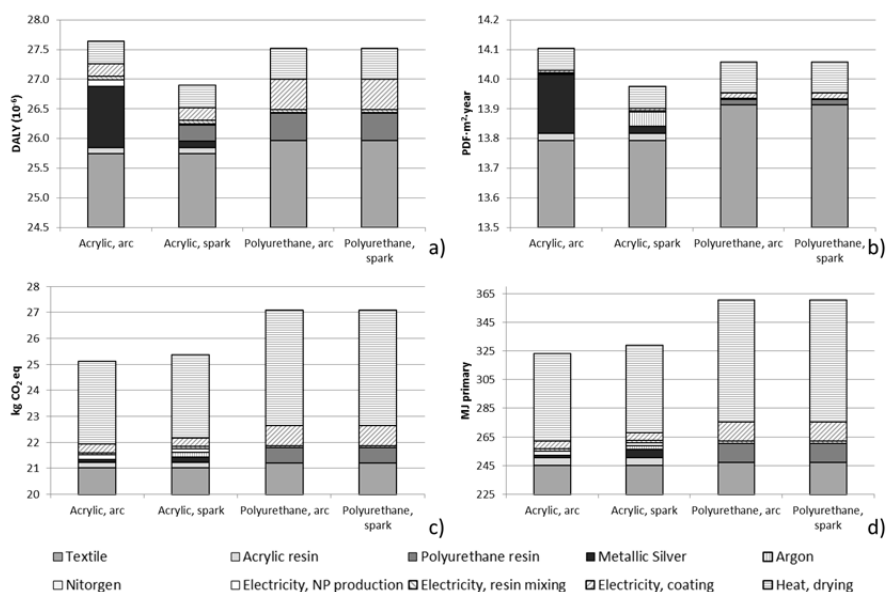
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Figure 17 Environmental impacts calculated for impact categories a) Human Health, b) Ecosystem quality, c) Climate change and d) Resource depletion for Ag NP in cotton for arc and spark generated NP, respectively.

The largest contribution to the environmental impact, in all four impact categories, for producition of cotton textile treated with Ag NP resin paste comes from the production of the cotton textile, as can be seen in Figure 17. The higher concentration of Ag NP in the cotton textile treated with acrylic paste is clearly visible in the Human health and Ecosystem quality categories, in which the production of the metallic Ag is the second largest contributor to the environmental impact. In all the other cases, the use of natural gas fired heat to dry the textile after resin coating contributes the most to the environmental impact in all categories. Electricity used by the equipment that mixes the NP with the resins and for the coating step has a small impact compared to the textile.

The results for the LCA study for silver nano-coated cotton textile using both acrylic and polyurethane resin and arc and spark produced NPs are shown in Table 9. The environmental impact is dominated by the impacts of the textile and resins, while the production method used for the NP production had a minimal impact. The impact of the final product was mainly dependent on which resin was used as binder. The use of polyurethane resin compared to acrylic resin has a slightly higher environmental impact.

Table 9 Environmental impact of nano-silver coated cotton textile. [Paper V]

Silver nano-coated cotton textile (1 kg of final product)	Human health DALY	Ecosystem quality PAF m² yr	Climate change kg CO_2 eq	Resource depletion MJ Primary
Acrylic resin, Arc NP	$3.21 \cdot 10^{-5}$	16.39	29.22	376.22
Acrylic resin, Spark NP	$3.11 \cdot 10^{-5}$	16.21	29.10	374.01
Polyurethane resin, Arc NP	$3.17 \cdot 10^{-5}$	16.19	31.24	415.62
Polyurethane resin, Spark NP	$3.17 \cdot 10^{-5}$	16.19	31.24	415.61

When comparing these results for the production and integration of the silver nanoparticles to the textiles to previously reported results by Walser et al. (2011) for t-shirts treated with silver nanoparticles the results are comparable. Of main interest in that study was the global warming impact, 0.20 kg CO_2 equivalents were released during the production of the coating for one t-shirt. The silver NP content in the coating was reported to be 0.021 g per T-shirt. For the process reported here, the CO_2 equivalents released for the production of acrylic resin containing the same amount of NP silver was 0.0000577 kg CO_2 equivalents. The impact of producing the resin coating for the cotton textile has a significantly lower impact compared to the T-shirt coatings. Similar evaluations for Zn in PP and Cu in cooling water have been carried out and can be found in Paper V and VI.

4.3. Scale-up

In this section the scale-up goals, the way forward and challenges that need to be overcome for the processes are discussed as well as at what technology readiness level each of the processes is. This is done to give a clearer picture of at what stage the processes are and how much work is still needed before the processes can be utilized industrially.

4.3.1. Scale-up of CCSM routes

A full industrial scale process would need to be able to process up to a megaton of serpentinite per year in order to be able to capture and sequester the CO_2 from a large CO_2 producing plant. So far laboratory experiments for the process have only been carried out as batch experiments as opposed to the continuous process envisioned. The scale at which the laboratory tests have been carried out is much smaller, with batches of a few tens of grams of serpentinite processes compared to the over 300 ton per hour required for the industrial scale. Before designing an industrial scale plant, a pilot plant needs to be designed and tested. One pilot plant has been envisioned to be built next to a lime kiln at Parainen where it would capture CO_2 from the flue gas. The full flue gas stream is too large for a pilot scale plant and, therefore, the CO_2 would be captured for a flue

gas side-stream. The envisioned scale of such a pilot plant would aim to process 550 kg/h serpentinite, taken from the Hitura nickel mine, to $Mg(OH)_2$ and 620 kg/h kiln gas. The pilot plant scale would be 70 times larger than the experiments carried out at lab-scale, Paper I. Alternatively magnesium containing rock from Vammala could be used, as reported by Koivisto et al. (2016), or possibly magnesium containing rock found in Parainen. Another possible site for a pilot plant would be at SSABs kiln in Raahe and using magnesium containing rock from the Hitura mine.

In addition to direct equipment related issues and the improvement of the energy use and efficiency of the process together with finding the correct operating parameters, other challenges need to be overcome. Among these are the corrosive nature of the fluids in the process, the risk of salt build-up and scaling, inlet flue gas composition, high pressure and temperatures in some of the process steps and high solids content in liquids. One of the main challenges with the scale up of the process will be the design of the serpentinite/ammonium sulphate reactor for the extraction of magnesium from the sepentenite rock. The ammonium sulphate and serpentinite rock are continuously fed into the first part of the extraction reactor. After that they are mixed and heated up to ~400-440°C. The gases released during the reaction are to be recovered for use at later stages of the process. This requires a gas tight reactor and feeding mechanism and solids extraction after the reactor. The serpentinite conversion reaction is endothermic and requires an external source of heat. Hot flue gas taken from the lime kiln can cover the heat demand. However, indirect heat exchange is required, as the flue gas cannot be in direct contact with the solids since this would introduce unwanted gas components to the reactor that would interfere with the conversion reactions. The reaction gas, mainly consisting of ammonia leaving the serpentinite/AS reactor, has a temperature of ~440°C. For efficient operation of the solid/solid reactor the temperature needs to be maintained at the optimum temperature, as AS salt starts to decompose into ammonia and ammonium bi-sulphate at too high temperatures. This may lower the extraction yield of Mg and production of $MgSO_4$ which is the desired product of the reactor.

The dissolution tank can be constructed in a straightforward fashion, as it requires nothing more complicated than a tank of water and a conveyor to remove the undissolved solids from the bottom. Solution containing dissolved iron and magnesium is led to two sequential precipitators where solubility of the metals is adapted by a change in pH. This is done by introducing the gaseous ammonia captured from the magnesium extraction reactor. To avoid the loss of

ammonia to the atmosphere the precipitators need to be gastight. In the first precipitation tank the pH is raised to ~8-9 and in the second to ~10-12. Here online measurement of pH and process control is important to ensure that the resulting particles are of a suitable particle size distribution and quality (i.e. specific surface) for the carbonation, as studied by Fagerlund (2012). The process requires that solid particles are removed from aqueous streams in both precipitation tanks and in the dissolution tank. In order to reduce the loss of solution it is important that the solids leaving the process contain as little liquid as possible. This can be achieved by using equipment such as heated press filters. In order for the lime kiln flue gas to be available as a heat source for the extraction reactor it has to be taken from the end of the kiln in order for it to be hot enough, as reported by Nordkalk (2011). As the gas contains steam and particulate matter, special considerations need to be made before it can be used as a heat source. The steam, particles and other possible unwanted components need to be removed before it can be compressed before CO_2 sequestration in the carbonation reactor. This could possibly be solved by feeding the gas used for heating back into the main flue gas channel for treatment before being extracted again for carbon capture.

The pilot scale fluidized bed reactor, as mentioned above, would have an inner diameter of about 10 cm and a height of 3 m for the first level of scale-up considered, compared to the 1.6 cm diameter and 0.5 m high lab scale reactor used in the lab, Fagerlund and Zevenhoven (2011) and Fagerlund (2012).

When scaling up and planning a pilot plant according to the ÅAU alternative route most of the challenges associated to the scale-up and planning of the pilot plant according to the conventional route would need to be overcome. The main differences are that there is no need for a compression and expansion system for the flue gas or a pressurized fluidized bed reactor. As there is no heat recovery from the carbonation reactor in the ÅAU alternative route, all the heat for the magnesium extraction reactor needs to be covered externally. In addition to this, the collection and possible transport of the product would be more challenging as the mass of product is higher per ton captured CO_2 is significantly larger.

The scale of the pilot plant causes complications. Readily available industrial equipment is too large, while laboratory equipment is much too small. Thus, finding equipment of usable size is difficult, if not impossible. If the issues discussed above cannot be resolved using standard industrial approaches and equipment, then special materials and equipment will be needed for several of

the process steps, adding considerable costs to this CCUS/CCSM process. Currently finding funding for the construction of a pilot scale (one of the first worldwide as reported by Pasquier et al. (2016)) CCUS/CCSM process according to the process presented here has proven to be difficult.

4.3.2. Scale-up of nanoparticle production process

The NP production process is to be scaled-up by constructing multiple arc or spark units, in parallel, in one housing while the other equipment is in general scaled-up by increasing the size of the equipment. This is a mix of the classic and linear scale-up procedures. The parallelization of multiple arcs follows the linear scale-up procedure (a linear increase in resources gives a corresponding linear increase in throughput) in terms of costs. However, for most of the other parts of the setup a classic scale-up is applicable where an increase in equipment size gives a higher throughput at a lower cost per product unit mass giving a benefit of scale. This is commonly known as economy of scale-up. Parts and equipment that benefit in this manner are for example the reactor housing, gas circulation pump and NP filtration unit and monitoring equipment. Particle monitoring equipment is classically scalable, because a single instrument is sufficient for a production plant and the monitoring cost per produced mass would decrease. Monitoring of the process can also be classically scalable due to the use of multiplexing so that a single detector can be used for many electrode pairs.

As seen in Table 3, the scale-up from OSU to mOSU showed no significant differences in SEC and only a small difference in collection rate. This would indicate that the scale-up follows a linear process, by addition of or numbering up the OSUs or mOSUs until the required production rate is obtained, see Stein and Kruis (2016) and BUONAPART-E (2016b). As the SEC of the power supplies for each arc is independent of scale, the main parameters that affect the efficiency of the scaled up process is the bulk metal-to-NP production efficiency and electricity use for gas circulation and cooling. For all three metals Ag, Cu and Zn studied in more detail, much can be gained if electricity consumption (i.e. cooling needs) can be reduced. For silver, however, it may be challenging to be competitive with conventional (wet chemistry) NP production, although the use of an arc or spark discharge system offers the opportunity of substituting for the use complex chemicals, [Paper IV].

The full-scale production setup would consist of 192 coupled OSUs into one production OSU (prOSU). A schematic picture of such a setup can be seen in Figure 18. The OSUs are setup in 24 mOSUs each consisting of 8 OSUs equally

spread out on three floors. This full-scale production unit would have the production capacity of 100 kg of metallic NP per 24 hours.
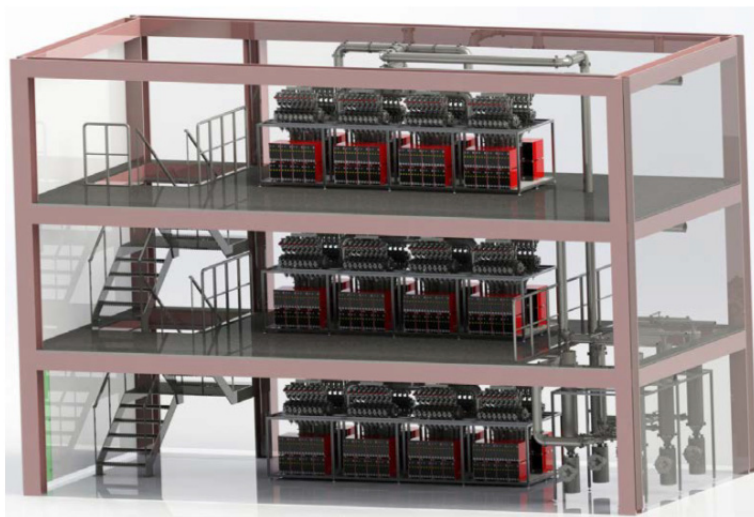

Figure 18 Overview of full-scale production facility (prOSU) consisting of 192 OSU equally distributed on three floors (Final report BUONAPART-E)

4.3.1. Technology readiness levels of CCSM routes and nanoparticle production by discharge evaporation

Different CCS/CCUS/CCSM technologies are at different TRLs. In general, solvent-based post-combustion CCS technologies have TRLs between 3 and 6, sorbent-based technologies have a TRL of 2 to 5 and membrane systems 3 to 5. The CCSM process developed at Åbo Akademi University is at TRL-4, moving to TRL-5. The process has been rigorously tested in laboratory scale in a batch-setup with synthetic flue gas, but a continuously operated process-setup starting from the magnesium extraction and ending with the carbonation has not been constructed or tested.

In contrast to the CCSM process, the NP production technology is at a higher TRL. The currently existing NP production test unit located in Duisburg-Essen, Germany, is of pilot plant scale and is slightly over 8% of the final industrial scale facility. This would give a TRL of 7.

5. Conclusions

All six of the research goals set for this thesis were met with most of the results published in articles and some in this thesis. It was found that the use of energy efficiency calculations and LCA are valuable tools when evaluating a process for future industrial application. They show where the processes need to be improved in order to create efficient and environmentally friendly processes and how they compare to already existing processes.

The first and third goals were met by the work reported in Paper I and II. For this, the optimum process variables and process setups were identified. Using exergy analysis to evaluate the energy efficiency when optimizing the heat integration of the CCUS/CCSM process with a lime kiln improved the heat economy of the process by slightly over 30%. This is a significant improvement. The optimized process was able to capture and sequester 187 kg CO_2/h while processing 550 kg rock per hour using 486 MJ of heat and 166 MJ of power. This translates into 2.59 MJ and 0.88 MJ per kg CO_2. Finally, for the alternative ÅAU route the overall exergy demand is 2930 MJ heat to sequester the same amount of CO_2 which translates into 15.4 MJ per kg CO_2. There are several equipment-related problems that need to be addressed and solved before an industrial scale CCUS/CCSM plant of the above described process can be designed and built. Even though many of these and many of the operating parameters for continuous operation have been discussed above to some extent, some issues regarding the process and the equipment still need to be solved. Among these are the corrosive nature of the fluids in the process, the risk of salt build-up and scaling, inlet flue gas composition, high pressure and temperatures in some of the process steps and high solids content in liquids.

The second research goal was met by the work presented in Paper III where it was found that the ÅAU route for CCSM is GHG negative when the heating demand can be covered by the utilization of waste heat. Per one kilogram of CO_2 sequestered the net amount of reduced CO_2 emissions is 0.445 kg CO_2 which corresponds to ~44.5 %. The main cause of GHG emissions from the CCSM process comes from the compression of the flue gas to the required 80 bar(g) for fast carbonation of the $Mg(OH)_2$ and the transport of the serpentinite rock from the mine to the carbonation plant. For the ÅAU alternative route per kilogram CO_2 sequestered the net amount of reduced CO_2 emissions is 0.74 kg CO_2, which corresponds to 74 %. Here the transportation of the serpentinite rock to the CCSM plant is the largest source of GHG emissions. When comparing the dry carbonation route with the wet carbonation route, it became clear that the wet carbonation route has a much smaller environmental

footprint, despite the higher energy input requirements. In the Human health, Ecosystem quality and Resource depletion categories, the environmental impact of the wet carbonation route is almost half of that for the dry carbonation route, while the CO_2 reduction in the Climate change category is almost double.

The work presented in Paper IV-VI covered the three remaining goals. Energy efficiency was evaluated for both laboratory scale and pilot scale setups in Paper VI. The scale-up of the process was done by parallelization of multiple OSU units into one larger facility. A lot of data was collected during the NP production experiments done with both arc and spark setups in both lab and pilot scales. By analysing the data with the use of exergy analysis together with heat measurements it was found that almost all of the power fed to the OSU or mOSU systems leaves the system as cooling heat instead of creating particle surface energy. As a result of this, the energy requirement of the process is several orders of magnitude higher than that suggested by the thermodynamic minimum energy. For copper NP of ~ 50 nm the measured SEC was ~ 250 kWh/kg, while the calculated minimum is 0.06 kWh/kg. There seems to be a clear correlation in the SEC needed to produce one gram of NP as a function of primary particle size, unlike the production of primary particle surface area. Small setups with short tubing have the highest yields, while the larger setups with more tubing have lower yields. The additional tubing in an mOSU setup leads to increased material losses, this in turn leading to a higher life cycle impact compared to an OSU. By optimizing the flow profile in the tubing and by directly minimizing the tubing the collection rate can be significantly improved. The cooling of the reactors and carrier gas should be done in a different way, so that the heat could be used directly or by the use of a heat pump for example for district heating or by some other means of utilizing the heat. By improving the material yield and reducing the amount of exergy lost by too low, close to ambient, temperature cooling the energy efficiency and the life cycle impact of the process can be improved greatly. The collected data also shows that scaling up the NP production by parallelization of OSUs is a valid approach, as the SEC remains similar for an mOSU compared to an OSU.

Performing the LCAs of the NP production routes was more difficult, as very little has been published on the synthesis of pure metallic NPs and the environmental effect they have. Therefore, the processes studied during the BUONAPART-E project were compared to processes described in literature with sufficient data available. This was done in Paper IV. The absolute values for the different impact categories were not the main focus in this study, but emphasis was placed on the comparison of the different methods. In general, it

was shown that the dry arc/spark process had a lower environmental impact than the wet chemical routes for Ag, Cu and Zn, but for Al the wet chemical route had a lower environmental impact.

Three NP-containing products were studied with LCA, but here the goal was to compare the different sources of environmental impact of the production of the product in Paper V. For the cotton treated with NP-containing resin it was shown that the main contribution to the environmental impact, in all four impact categories, for producing of cotton textile treated with Ag NP resin paste comes from the production of the cotton textile. The higher concentration of Ag NP in the cotton textile treated with acrylic paste is clearly visible in the Human health and Ecosystem quality categories, in which the production of the metallic Ag is the second largest contributor to the environmental impact. In all the other cases, the use of natural gas fired heat to dry the textile after resin coating contributes the most to the environmental impact in all categories. Electricity used to mix the NP with the resins and for the coating step has a small impact compared to the textile. The carrier gas used during the synthesis of the NP had a negligible effect on the environmental impact of the product. When comparing those results for the production and integration of the silver nanoparticles to the textiles to that previously reported for T-shirts treated with silver nanoparticles, the results were comparable. Of main interest in that study was the global warming impact, 0.20 kg CO_2 equivalents were released during the production of the coating for one t-shirt. The silver NP content in the coating was reported to be 0.021 g per T-shirt. For the process studied during the BUONAPART-E project, the CO_2 equivalents released for the production of acrylic resin containing the same amount of NP silver was 0.0000577 kg CO_2 equivalents. The impact of producing the resin coating for the cotton textile has a significantly lower impact compared to the T-shirt coatings.

Based on the improvements to both studied processes made possible by the use of energy efficiency evaluation and life cycle assessment while evaluating the processes, it is clear that these methods can be successfully applied to processes of different scales. Even though the maturities of both processes have improved during the work reported on in this thesis, they both appear not mature enough for full industrial implementation. The NP production process is closer to maturity, as the process has already been tested in pilot scale. This is partly because of the much smaller scale of the pilot plant for the NP process compared to the CCUS process. The NP pilot process can produce up to 70 g/h, while the envisioned CCUS pilot would process over 550 kg of serpentinite rock per hour and capture 180 kg CO_2 per hour. To receive funding for the

construction of the much larger CCUS pilot has so far proved to be difficult, mainly because the costs of CO_2 emissions under the European trading scheme (ETS) for CO_2 make CCS/CCUS/CCSM economically unattractive, even when considering the market value of the solid product of CCSM.

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