

Utilization of steelmaking waste materials for production of calcium carbonate (CaCO_3)

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Preface

The research work presented in this thesis was conducted mainly as a part of the Carbon Capture and Storage Program (CCSP, 2011-2015) coordinated by CLEEN Ltd., with funding from the Finnish Funding Agency for Technology and Innovation, Tekes. Program partners at Outotec Research Center and Ruukki Metals Oy provided valuable information of the industrial processes. Financial support was received from the Graduate School in Chemical Engineering, Walter Ahlströms foundation, and Lixivia, Inc. All of these institutions are gratefully acknowledged.

However, this book, one in a series of theses addressing mineral carbonation, would not have been written without Professor Ron Zevenhoven, under whose supervision I continued the work initiated during my masters' thesis studies. I'm thankful of his guidance and valuable discussions, which I have been able to enjoy already since October 2008.

All the personnel at Thermal and Flow Engineering Laboratory have always been extremely helpful and supported my research work. This includes Henrik, Frank, Affi, Vivéca and my co-authors Inga, Sami and Hannes, as well as other colleagues and friends with whom we have spent a lot of time together: Johan, XP, Inês, Martin, Martin, Calle, Daniel, Debanga, Evelina, Markéta, Raine, Ramkrishna, Tamoghna and all the others. Without you these years would have been quite boring and difficult. Discussions with co-workers at Aalto University, Sanni, Arshe, and Will have always been inspiring for new thoughts and ways of thinking. I was also privileged to spend two months in Santa Barbara, California, as a visiting researcher at Lixivia, Inc., the lab of Mike Wyrsta and Zach Komon. A great thanks to all of you.

Naturally, I also thank my parents, who have always supported me and believed in me. Thank you!

Svensk sammanfattning

Stålindustrin producerar förutom stål också fasta biprodukter, eller slagg, medan den släpper ut stora mängder koldioxid (CO_2) i atmosfären. Slagg består av olika silikater och oxider, vilka bildas i kemiska reaktioner mellan järnmalm och slaggbildare under högtemperaturprocesserna i ståltillverkningen. För närvarande, återanvänds dessa material i masugnen, utnyttjas som byggmaterial, eller deponeras som avfall.

En större del av stålslaget kunde utnyttjas genom att selektivt extrahera valda komponenter från mineralmatrisen. Exempelvis, vattenlösningar av ammoniumsalter, såsom ammoniumacetat, -klorid och -nitrat, extraherar kalcium mycket selektivt redan vid atmosfäriskt tryck och omgivningens temperatur. När de kvarstående fasta ämnen har separerats från lösningen kan kalciumkarbonat fällas ut genom att mata ett CO_2 -gasflöde genom lösningen.

Utfällt kalciumkarbonat (precipitated calcium carbonate, PCC) används i olika tillämpningar som ett fyllnadsmedel. Pappersindustrin, som använder PCC för att förbättra papprets optiska egenskaper med relativt låga kostnader, är den största konsumenten. Traditionellt tillverkas PCC av kalksten, som först kalcineras till kalciumoxid, sedan släcks med vatten till kalciumhydroxid och slutligen karbonatiseras till PCC. Denna process avger stora mängder CO_2 , främst på grund av det energikrävande kalcineringssteget.

Denna avhandling presenterar vetenskapligt forskning gällande uppskalning av den ovannämnda metoden baserad på ammoniumsalter för extrahering och karbonatisering av kalcium. Metoden kallas för Slag2PCC. Som utvidgning av de tidigare resultaten, bevisas det nu att de parametrar som mest påverkar kalciums extraheringseffektivitet är förhållandet av slagg och lösningsmedel vid extraheringsreaktionen, medeldiametern av slaggpartiklarna och slaggsammansättningen, speciellt fraktionerna av kalcium, kisel, vanadin och järn samt fraktionen av fri kalciumoxid. Slaggets partikelstorlek, slaggvätskeförhållandet och lösningsmedelkoncentrationen har den största inverkan till reaktionshastigheten vid extraheringen.

Lösningsmedelkoncentrationer högre än 1 mol/L främjar lakning av andra element förutom kalcium. En del av dessa, som järn och mangan, färgar processlösningen, vilket kan vara ofördelaktigt för PCC-produktkvaliteten. När den kemiska sammansättningen av producerat material har analyserats, har inga större skillnader jämfört med kommersiella PCC-produkter hittats.

Som förstärkning av arbetets originalitet, andra viktiga parametrar relaterade till bedömningen av PCC-kvaliteten, nämligen partikelstorleksfördelningar och kristallmorfologin, undersöks också. Såsom i traditionella PCC-utfällningsprocesser, styr förhållandet av kalcium- och karbonationer partikelformen; högre $[\text{Ca}^{2+}]/[\text{CO}_3^{2-}]$ -värde främjar utfällning av kalcit, medan vaterit bildas vid överskott av koldioxid. Den tredje primära kristallformen, aragonit, bildas endast vid temperaturer över 40-50 °C.

Allmänt, längre reaktionstider får vaterit att omvandlas till kalcit eller aragonit, medan de också förorsakar agglomerering av de enskilda partiklarna. Den kemiska jämvikten mellan ammonium- och kalciumjoner samt upplöst ammoniak, vilken kontrollerar lösningens pH-värde, påverkar också partikelstorlekarna. Begynnelsevärden för pH 12-13 i karbonatiseringen gynnar utfällning av icke-agglomererade partiklar med diametrar av 1 μm och mindre, medan pH-värdena 9-10 producerar agglomerat av 10-20 μm .

Som en del av forskningsarbetet, har dessa upptäckt tillämpats i experimentella demonstrationsanläggningar. Olik förr, har Slag2PCC-teknologin provkörts i en process av ~ 70 liter i stället för endast laboratorieskala. En process av flera hundra liter har också utvecklats. Olika processteg och -utrustning, exempelvis lutande sedimenteringskärn och filter för separering av fasta partiklar, pumpar och blandare för materialtransport och -blandning samt gasinmatningsutrustning, har dimensionerats för dessa ändamål.

Med minskning av utsläppen från industriella processer och säkerställning av den goda produktkvaliteten som de viktigaste målen, är det, utgående från den utförda partiella livscykelanalysen (LCA), fördelaktigt att använda ammoniumsaltlösningar med låg koncentration i Slag2PCC-processen. Detta medför att man inte behöver efterbehandla produkterna med tvättnings- och torkningssteg, vilka skulle öka processens CO_2 -utsläpp.

Slag2PCC-processen med låg lösningsmedelkoncentration har negativa CO_2 -utsläpp; därför kan denna teknologi ses som en avskiljnings- och användningsmetod för koldioxid (carbon capture and utilization, CCU), vilket egentligen minskar de antropogena CO_2 -utsläppen jämfört med alternativet att inte utnyttja tekniken. Mängden stålslag är för liten för en signifikant inverkan på den globala uppvärmningen, men processen kan ha betydelse gällande både ekonomiska och miljöfrågor för enskilda ståltillverkare eftersom den kan utnyttjas för att minska mängderna av utsläppt CO_2 och deponerat stålslaggavfall.

Alternativt är det möjligt att mata in koldioxiden direkt i blandningen av stålslagget och ammoniumsaltlösningen. Processen skulle då tillverka en 60-75 % ren kalciumkarbonatblandning, där resten skulle bestå av det kvarstående stålslagget. Detta kalciumrika material kan återanvändas i järnframställningen som slaggbildare istället för naturlig kalksten. Även om detta processalternativ skulle kräva mindre processutrustning jämfört med Slag2PCC-processen, måste den praktiska användbarheten av produkterna studeras vidare.

Ändå, jämfört med flera andra metoder för minskning av koldioxidutsläppen, som flitigt studeras runt världen, har dessa, inom denna avhandling utvecklade och studerade processer den fördelen att det åtminstone i princip finns marknader för produkterna, vilket ger en ekonomisk grund för att tillämpa tekniken i praktik.

Abstract

The steel industry produces, besides steel, also solid mineral by-products or slags, while it emits large quantities of carbon dioxide (CO_2). Slags consist of various silicates and oxides which are formed in chemical reactions between the iron ore and the fluxing agents during the high temperature processing at the steel plant. Currently, these materials are recycled in the ironmaking processes, used as aggregates in construction, or landfilled as waste.

The utilization rate of the steel slags can be increased by selectively extracting components from the mineral matrix. As an example, aqueous solutions of ammonium salts such as ammonium acetate, chloride and nitrate extract calcium quite selectively already at ambient temperature and pressure conditions. After the residual solids have been separated from the solution, calcium carbonate can be precipitated by feeding a CO_2 flow through the solution.

Precipitated calcium carbonate (PCC) is used in different applications as a filler material. Its largest consumer is the papermaking industry, which utilizes PCC because it enhances the optical properties of paper at a relatively low cost. Traditionally, PCC is manufactured from limestone, which is first calcined to calcium oxide, then slaked with water to calcium hydroxide and finally carbonated to PCC. This process emits large amounts of CO_2 , mainly because of the energy-intensive calcination step.

This thesis presents research work on the scale-up of the above-mentioned ammonium salt based calcium extraction and carbonation method, named Slag2PCC. Extending the scope of the earlier studies, it is now shown that the parameters which mainly affect the calcium utilization efficiency are the solid-to-liquid ratio of steel slag and the ammonium salt solvent solution during extraction, the mean diameter of the slag particles, and the slag composition, especially the fractions of total calcium, silicon, vanadium and iron as well as the fraction of free calcium oxide. Regarding extraction kinetics, slag particle size, solid-to-liquid ratio and molar concentration of the solvent solution have the largest effect on the reaction rate.

Solvent solution concentrations above 1 mol/L NH_4Cl cause leaching of other elements besides calcium. Some of these such as iron and manganese result in solution coloring, which can be disadvantageous for the quality of the PCC product. Based on chemical composition analysis of the produced PCC samples, however, the product quality is mainly similar as in commercial products.

Increasing the novelty of the work, other important parameters related to assessment of the PCC quality, such as particle size distribution and crystal morphology are studied as well. As in traditional PCC precipitation process, the ratio of calcium and carbonate ions controls the particle shape; a higher value for $[\text{Ca}^{2+}]/[\text{CO}_3^{2-}]$ prefers precipitation of calcite polymorph, while vaterite forms when

carbon species are present in excess. The third main polymorph, aragonite, is only formed at elevated temperatures, above 40-50 °C.

In general, longer precipitation times cause transformation of vaterite to calcite or aragonite, but also result in particle agglomeration. The chemical equilibrium of ammonium and calcium ions and dissolved ammonia controlling the solution pH affects the particle sizes, too. Initial pH of 12-13 during the carbonation favors non-agglomerated particles with a diameter of 1 µm and smaller, while pH values of 9-10 generate more agglomerates of 10-20 µm.

As a part of the research work, these findings are implemented in demonstration-scale experimental process setups. For the first time, the Slag2PCC technology is tested in scale of ~70 liters instead of laboratory scale only. Additionally, design of a setup of several hundreds of liters is discussed. For these purposes various process units such as inclined settlers and filters for solids separation, pumps and stirrers for material transfer and mixing as well as gas feeding equipment are dimensioned and developed.

Overall emissions reduction of the current industrial processes and good product quality as the main targets, based on the performed partial life cycle assessment (LCA), it is most beneficial to utilize low concentration ammonium salt solutions for the Slag2PCC process. In this manner the post-treatment of the products does not require extensive use of washing and drying equipment, otherwise increasing the CO₂ emissions of the process.

The low solvent concentration Slag2PCC process causes negative CO₂ emissions; thus, it can be seen as a carbon capture and utilization (CCU) method, which actually reduces the anthropogenic CO₂ emissions compared to the alternative of not using the technology. Even if the amount of steel slag is too small for any substantial mitigation of global warming, the process can have both financial and environmental significance for individual steel manufacturers as a means to reduce the amounts of emitted CO₂ and landfilled steel slag.

Alternatively, it is possible to introduce the carbon dioxide directly into the mixture of steel slag and ammonium salt solution. The process would generate a 60-75% pure calcium carbonate mixture, the remaining 25-40% consisting of the residual steel slag. This calcium-rich material could be re-used in ironmaking as a fluxing agent instead of natural limestone. Even though this process option would require less process equipment compared to the Slag2PCC process, it still needs further studies regarding the practical usefulness of the products.

Nevertheless, compared to several other CO₂ emission reduction methods studied around the world, the within this thesis developed and studied processes have the advantage of existing markets for the produced materials, thus giving also a financial incentive for applying the technology in practice.

List of publications

The publications presented at the end of this thesis will be referred to using the Roman numerals given in the following list.

- I. **Production of precipitated calcium carbonate from steel converter slag and other calcium-containing industrial wastes and residues**
H.-P. Mattila, R. Zevenhoven
Chapter 10 in M. Aresta, R. van Eldik, editors: “Advances in Inorganic Chemistry Vol. 66: CO₂ Chemistry”, Burlington: Academic Press, 2014, pp. 347-384. DOI: 10.1016/B978-0-12-420221-4.00010-X
- II. **Chemical kinetics modelling and process parameter sensitivity for precipitated calcium carbonate production from steelmaking slags**
H.-P. Mattila, I. Grigaliūnaitė, R. Zevenhoven
Chem. Eng. J., 2012, 192, pp. 77–89. DOI: 10.1016/j.cej.2012.03.068
- III. **Process efficiency and optimisation of precipitated calcium carbonate (PCC) production from steel converter slag**
H.-P. Mattila, I. Grigaliūnaitė, A. Said, S. Filppula, C.-J. Fogelholm, R. Zevenhoven
Paper 114 (peer-reviewed) in The 25th International Conference on Efficiency, Cost, Optimization and Simulation of Energy Conversion Systems and Processes (ECOS), 2012, June 26-29, Perugia, Italy. Book of Proceedings, Vol. 6. pp. 218-232.
- IV. **Design of a continuous process setup for precipitated calcium carbonate production from steel converter slag**
H.-P. Mattila, R. Zevenhoven
ChemSusChem, 2014, 7, pp. 903–913, DOI: 10.1002/cssc.201300516
- V. **Cradle-to-gate life cycle assessment of precipitated calcium carbonate production from steel converter slag**
H.-P. Mattila, H. Hudd, R. Zevenhoven
Journal of Cleaner Production, 2014, DOI: 10.1016/j.jclepro.2014.05.064
- VI. **Reduced limestone consumption in steel manufacturing using pseudocatalytic calcium lixiviants**
H.-P. Mattila, M.D. Wyrsta, R. Zevenhoven
Energy & Fuels, 2014, 28(6), pp. 4068-4074. DOI: 10.1021/ef5007758

Contribution of the author

The author of this thesis has designed and performed most of both the experimental and theoretical work presented in these publications. In Papers II and III the co-authors participated both in experimental work as well as in writing of the papers. The construction of the experimental setup presented in detail in Paper IV has also been performed by the author, with the valuable help of colleagues and various specialists. The one-step carbonation method discussed in Paper VI is based on ideas of Dr Wyrsta.

Related publications

Besides the above listed contributions, the author of this thesis has participated in conferences and meetings with non-reviewed publications, reports and presentations, as listed below, on the field of steel slag utilization as well as on carbon dioxide sequestration. Also a journal article published in collaboration with colleagues at Aalto University, Espoo, Finland is included in this list.

- VII. **Scale-up and optimisation of production of precipitated calcium carbonate from steelmaking slag**
H.-P. Mattila, R. Zevenhoven
11th International Conference for Carbon Dioxide Utilization (ICCDU)-XI, 2011, June 27-30, Dijon, France. Book of Abstracts, OC73, p. 91.
- VIII. **Production of papermaking grade calcium carbonate from steelmaking slag – product quality and development of a larger scale process**
H.-P. Mattila, I. Grigaliūnaitė, A. Said, C.-J. Fogelholm, R. Zevenhoven
Proceedings of SCANMET IV – 4th International Conference on Process Development in Iron and Steelmaking, 2012, June 10-13, Luleå, Sweden. Book of Proceedings, Vol. 2. pp. 19-28.
- IX. **BOF slag carbonation in aqueous NH₄Cl-solutions: steering product quality in a continuous process**
H.-P. Mattila, M. Slotte, A. Said, R. Zevenhoven
Proceedings of the 4th International Conference on Accelerated Carbonation for Environmental and Materials Engineering (ACEME), 2013, April 9-12, Leuven, Belgium. pp. 547-550.
- X. **Production of precipitated calcium carbonate (PCC) from steelmaking slag for fixation of CO₂**
A. Said, H.-P. Mattila, M. Järvinen, R. Zevenhoven
Appl. Energy, 2013, 112, pp.765-771. DOI: 10.1016/j.apenergy.2012.12.042
- XI. **Producing precipitated calcium carbonate (PCC) from steelmaking slags using the slag2pcc concept**
H.-P. Mattila, R. Zevenhoven
World Resources Forum 2014, October 19-22, Arequipa, Peru. *Accepted for oral presentation*, Paper ID66.

List of abbreviations and symbols

BOF	Basic oxygen furnace
CCUS	Carbon dioxide capture, utilization and storage
EN1.4521	A corrosion resistant steel quality
GCC	Ground calcium carbonate
LCA	Life cycle assessment
PCC	Precipitated calcium carbonate
SEM	Scanning electron microscope
Slag2PCC	Process concept for production of precipitated calcium carbonate from steel slags
USD	United States Dollar
ÅAU	Åbo Akademi University
Ca	Calcium
CaCl ₂	Calcium chloride
CaCO ₃	Calcium carbonate (calcite, aragonite, limestone)
CaO	Calcium oxide (free lime)
Ca(OH) ₂	Calcium hydroxide
CaSiO ₃	Calcium silicate (mineral name: wollastonite)
Ca ₂ SiO ₄	Dicalcium silicate (mineral name: larnite)
CO ₂	Carbon dioxide
CO ₃ ²⁻	Carbonate ion
HCl	Hydrochloric acid
NH ₄ Cl	Ammonium chloride
(NH ₄) ₂ CO ₃	Ammonium bicarbonate
NH ₄ OH	Ammonium hydroxide
<i>L_{gas}</i>	Litres of gas
<i>L_{liquid}</i>	Litres of liquid

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1. Introduction

Industrial waste materials can be utilized to partly replace existing production of calcium-rich materials such as calcium carbonate (CaCO_3), which currently is primarily based on natural resources. Examples of solid, calcium-containing waste streams suitable for carbonate production are different ashes, gypsum waste and cementitious materials as well as slags from steelmaking industry. (Paper I) This work focuses on usage of steel slags, in particular steel converter or basic oxygen furnace (BOF) slag, because of their high calcium content compared to several other alternatives. In addition, the Finnish steel industry generates large amounts of these by-products; in 2013 manufacturing of 2.2 Mt steel produced 0.47 Mt mineral aggregates, including materials that were utilized for construction and other purposes, and that were stored to be processed in the future.¹ Figure 1 represents the framework of this study in detail with respect to various industries such as steel- and papermaking. The estimated orders of magnitude of the different material flows are listed in the figure.

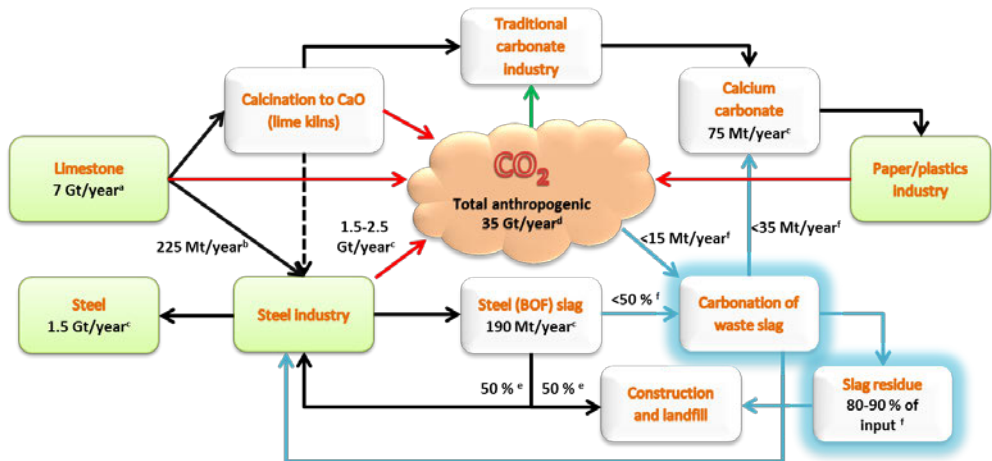


Figure 1. An overview of the industry branches studied within this research work. Numerical values indicate the order of magnitude for annual production of the various materials globally. The developed alternative process options are marked in blue.

^a Production of crushed rock, mainly limestone, annual estimate²

^b Limestone consumption in steelmaking³

^c Paper IV

^d Ref. ⁴

^e Ref. ⁵

^f Estimated based on mass balances of the other streams.

In calcium carbonate, calcium oxide (CaO) is bound to carbon dioxide (CO_2), a chemical at the moment widely debated because of its connection to climate change and global warming.^{6,7} If industrial wastes are used as calcium sources for CaCO_3 manufacturing, the process can be categorized as a carbon dioxide capture, utilization and storage (CCUS) technology. Traditional limestone-based CaCO_3 industry generates more CO_2 than which is later stored in the formed products because the calcium is in

carbonated form already before processing.⁸ When an alternative calcium source is used, calcium carbonate manufacturing simultaneously reduces the amounts of both CO₂ emissions and solid wastes. Because the iron and steel industry is a large CO₂ emitter, one advantage of using steelmaking slags for production of calcium carbonate would be the possibility of on-site “calcium recycling”, which could, in addition, reduce the need of material transport.

As commercial CaCO₃ products are relatively inexpensive (>60 USD/ton⁹), they are commonly used to replace more valuable raw materials in several applications. Examples of these are paints, plastics and paper, but calcium carbonate can be utilized as a nutritional supplement in animal foods as well.^{10,11} Depending on the required quality, CaCO₃ is either directly milled from limestone (Ground Calcium Carbonate, GCC) or treated further to remove the impurities.

The most common technology for production of high purity CaCO₃ with a well-defined particle size distribution and crystal morphology is the so-called carbonation process, generating Precipitated Calcium Carbonate (PCC).^{8,12} The limestone is first calcined at high temperatures (900-1000 °C), which removes the CO₂ from the solid material. Then, the formed calcium oxide is slaked with water, and this aqueous slurry is contacted with gaseous carbon dioxide, usually in a batch reactor. The discontinuous reaction enables straight-forward adjustment of parameters such as calcium concentration and gas flow rate, which affect the solution (super-)saturation and product precipitation via the nucleation rates. Also, reaction time, temperature, solution pH and mixing properties are accurately controlled. Thus, the crystallization can be steered and controlled to manufacture a product that fulfils the requirements set by the specified use.¹³⁻¹⁹ PCC market prices can be up to 350 USD/ton.⁹

The financial incentive of producing PCC from steelmaking slags and other calcium-containing industrial waste materials is higher compared to manufacturing low-quality CaCO₃. However, the challenge is to guarantee similar product properties as in traditional PCC production, regarding especially material purity. Steelmaking slags contain, besides calcium, several other elements such as iron, silicon, manganese, magnesium, aluminium and vanadium (Table 1, page 7). These form a mineralogical matrix of impure ferrous and aluminous calcium silicates (Table 2, page 7). Selective and efficient separation of calcium from this mixture is a necessary pre-requisite for successful precipitated calcium carbonate manufacturing (Table 4, page 11).

Earlier research has identified aqueous ammonium salt solutions, more specifically ammonium acetate, chloride and nitrate, as selective and efficient solvents or lixiviants for separating calcium from steelmaking slags.^{20,21} The slag used in these studies was mainly steel converter slag, obtained from a basic oxygen furnace (BOF) process at Ruukki Metals Oy in Raahе, Finland. Because certain particle size fractions of this waste stream lack a viable use in e.g. agriculture and construction,⁵ research work on PCC production has continued using different batches of the same material.

Depending on the slag mineralogy, 10-50 wt.-% of the calcium present in the slag has been dissolved in the experiments. Even the ammonium salt solvents, however, extract small amounts of other elements, such as silicon and magnesium, but also potassium and sodium. (Paper IV)

As in general in the process industry, it would be beneficial both for process economics and the environment to use a closed-loop system with continuous solvent recycling. With ammonium salt solutions for PCC production from BOF slag this approach is theoretically simple; the solvent salt is regenerated in the precipitation stage by introducing gaseous carbon dioxide to the calcium-rich solution that has been separated from the slag residue. At the same time the product, solid calcium carbonate, precipitates from the aqueous phase. This process concept, called Slag2PCC, can be operated at ambient pressure and at near-ambient temperatures, and is schematically presented in Figure 2.

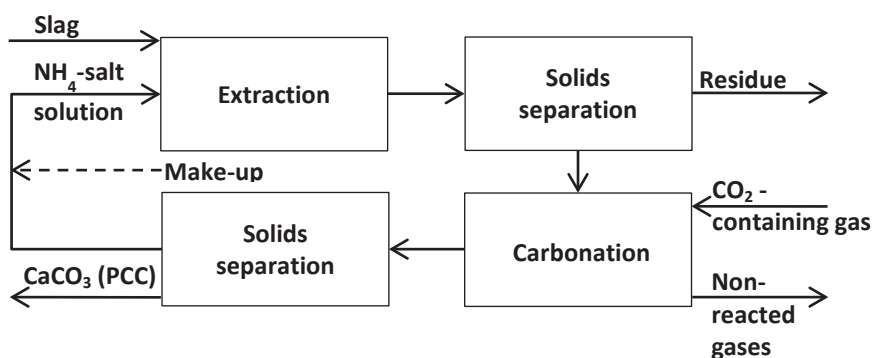


Figure 2. Process schema for precipitated calcium carbonate (PCC) production process, Slag2PCC, using BOF slag, gaseous carbon dioxide and ammonium salt solutions.

The main objective of this work is to optimize the Slag2PCC process with respect to following aspects by utilizing for example the listed scientific methods:

- Efficient utilization of Ca present in slag
 - Kinetic and thermodynamic studies of the calcium extraction step
- Production of commercial quality PCC
 - Kinetic and thermodynamic studies of the precipitation reaction, effects of various parameters on product purity as well as on particle size and morphology
- Efficient and minimized use of energy, water and solvent salt
 - Life cycle assessment (LCA) based comparison of various production methods
- Continuous and discontinuous operation including particle separation and process solution recycling,

- Practical dimensioning and developing the necessary process equipment such as settlers, pumps and mixers

In addition, developing a practically working mineral carbonation process would serve as a demonstration of similar type CCUS methods, which are currently being tested in lab-scale. Markets of calcium carbonate and the amounts of suitable solid wastes are limited compared to annual carbon dioxide emissions (Figure 1), but a successful commercial application could support the development of related technologies, being capable of more significant reduction of CO₂ emissions. Paper I presents a literature review of the existing PCC manufacturing methods and the recent research efforts to utilize different calcium-rich industrial wastes for production of carbonate materials and mitigation of the global climate change.

In Paper II results from kinetic studies of the Slag2PCC reactions are discussed. Instead of the long residence times, 120 min extraction and 60 min carbonation, used in earlier experimental work,²¹ reaction steps can be shorter. For extraction, the reactivity of the slag material defines a suitable residence time. Regarding carbonation, initial calcium concentration and CO₂ gas flow rate determine the time requirements, but in lab-scale the conversion can be completed in 10-20 min. Residence times of 25 to 60 min have been used in the on-going research for both reaction steps.

Papers III and IV discuss aspects such as operating the process in a continuous mode instead of batch processing as well as separation of solids from the process solutions. Additionally, the constructed experimental setup units are presented. It is noted that several parameters affect the calcium extraction efficiency; among these are the fractions of calcium, iron and silicon in slag, but also slag particle size and the chosen slag-to-liquid ratio.

Even though process solution recycling is an environmentally and economically feasible target, complete recovery and reuse of the solvent is challenging. Considerable amounts of ammonium salt solution leave the process both with the slag residue and the produced PCC, which are separated from the process solutions by using a pre-thickener – filter combination. In addition, ammonia vapors can leave the system together with the purge of unreacted gases from carbonation. Thus, a certain amount of make-up NH₄Cl solution is required to compensate for the losses caused by the wet product streams.

The losses can be decreased by washing the solids leaving the process. This is essential specifically for cleaning the produced PCC of the ammonium salt, which can then be reintroduced to the system together with a fraction of the washing water as a make-up stream. Possibly a gas scrubber is required to capture the ammonia vapors. These additional treatments increase the process water consumption while they also make the process more complex in general.

Paper V consists of a partial life cycle assessment (LCA) study comparing the environmental effects of the Slag2PCC method and the traditional carbonation process for PCC manufacturing. The results show that the material recycling aspects of the Slag2PCC approach result in environmental benefits such as reduced CO₂ emissions, despite of the more complex process chemistry, but only if the ammonium salt solvent recycling is performed in a feasible manner. Alternatively, a low solvent concentration Slag2PCC process can remove the need of solids washing.

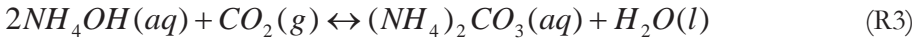
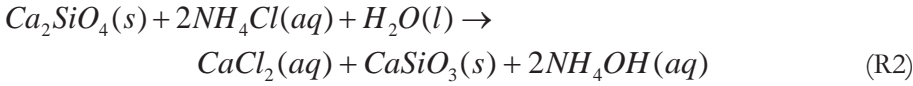
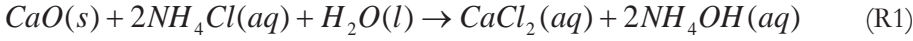
Besides product purity (Table 4), obtaining a commercial particle quality requires attention at the process design level. Because the concentrations of calcium and carbonate species as well as the solution pH in the carbonation stage (Papers II-IV) differ from those used in traditional carbonate manufacturing,¹³⁻¹⁹ the precipitated particles do not necessarily have the same morphology and particle size as the traditional PCC products. This problem can be solved by adjusting the process parameters in such a way that the commercial specifications are met, as discussed in later sections.

On the other hand, if production of high quality PCC is not aimed at, it is possible to manufacture less valuable GCC-quality products instead. An example of this approach is described in Paper VI. In this one-step process the product would consist of 60-75 wt.-% pure carbonate that could be used to partially replace limestone-based compounds in steelmaking. While the carbonation process would become simpler, the economic viability of the process could be challenged by the lower product value.

2. Main features of the Slag2PCC process

The principal chemical reactions of the Slag2PCC process are listed in Scheme 1. Of the various calcium-containing compounds present in steel slag only free lime (calcium oxide, CaO) and larnite (dicalcium silicate, Ca₂SiO₄) react to a larger extent with the here used ammonium salt solvent (Papers II-IV). Reactions R1-R2 describe the extraction step, while Reactions R3 and R4 occur during carbonation.

Scheme 1. Main chemical reactions of the Slag2PCC process.



The process chemistry is written for ammonium chloride, because that was used in most of the experiments. This choice is based on the lower calcium extraction performance of earlier tested ammonium acetate compared to chloride and nitrate, and on the legal limitations set on use and storage of ammonium nitrate in certain countries due to its explosive nature. Additionally, ammonium chloride is the cheapest of these three salts, and it has been previously used in similar work by Kodama et al.^{21,22}

In the following the effects of different process parameters on the Slag2PCC concept are presented, primarily based on Papers II-V.

2.1. Slag composition and particle size (Papers II, IV)

As mentioned, BOF slag is not a uniform material; both the elemental composition and the mineralogy vary depending on steelmaking process changes as well as on the after-treatment of the formed slag. Examples of the composition of the slag fractions used in experimental work are shown in Tables 1 and 2. In the Slag2PCC process the best overall calcium extraction efficiency is obtained by using slag with a high free lime content. Extraction is more hindered in slags with large silicon, vanadium or iron fractions. Outdoor storage may change the efficiency of calcium separation, which was studied with slag that had been 16 months outdoors. Calcium extraction efficiency was slightly lower than with slag that had been protected from rainwater and frost.

Table 1. XRF results of the various slag fractions (Paper IV)

[%]	CaO	Fe	SiO ₂	Mn	MgO	Al ₂ O ₃	V	Na ₂ O	P	S	K ₂ O	Ti	Cr	Rest
2008	45.2	14.9	12.4	2.4	1.7	1.5	1.4	0.1	0.4	0.1	0.1	0.6	0.2	19.0
2011	44.9	12.0	22.7	2.6	1.6	2.6	2.5	0.2	0.4	0.1	0.2	0.8	-	9.4
2011, aged, 10-50 mm	44.5	13.4	23.0	2.6	1.8	2.6	2.6	0.3	0.4	0.1	0.2	0.8	0.2	7.5
2011, aged, >300 mm	42.2	17.6	22.5	2.4	1.7	2.4	2.4	0.2	0.4	0.1	0.2	0.7	0.2	7.0
2012	42.4	17.7	11.9	2.1	1.4	1.5	1.3	0.1	0.3	0.1	0.1	0.7	0.3	20.2
2012b	47.5	17.4	11.7	2.6	1.8	1.4	1.3	0.1	0.3	0.1	0.1	0.7	0.2	14.8

Table 2. XRD results of the various slag fractions (Paper IV)

[%]	Lime (CaO)	Portlandite (Ca(OH) ₂)	Larnite (Ca ₂ SiO ₄)	Srebrodolskite (Ca ₂ Fe ₂ O ₅)	Calcium Magnesium Iron Silicate (Ca ₂ Fe _{1.2} Mg _{0.4} Si _{0.4} O ₅)	Quartz (SiO ₂)	Other
2008	5	-	59	26	-	-	10
2011 ^[a]	-	-	yes	yes	-	-	yes
2012	12	17	-	-	65	6	-
2012b	9	10	-	-	38	-	43
[a] No quantitative XRD analysis was performed on this material							

Table 3. The studied models representing the dissolution reaction of solid particles; α is the conversion (%) of solid form CaO, while $g_x(\alpha)$ is function x of α . The functions are labeled according to Grénman.²³

x	$g_x(\alpha)$	Type of model
	α	External mass transfer
1	$-\ln(1-\alpha)$	First-order kinetics
2	$(1-\alpha)^{-1/2} - 1$	Three-halves-order kinetics
3	$(1-\alpha)^{-1}$	Second-order kinetics
7	$[1-(1-\alpha)^{1/3}]^2$	Jander equation: three-dimensional diffusion, spherical symmetry
9	$[1/(1-\alpha)^{1/3} - 1]^2$	Zhuravlev–Lesokhin–Tempelman equation: three-dimensional diffusion, concentration of penetrating species varies with conversion (α)

All the slag material was crushed or sieved to a specified particle size fraction prior to experimental work. The original slag particle size (diameters >300 mm vs. 10-50 mm) before crushing had no significant effect on the calcium extraction efficiency, which indicates that the mineralogy and composition of the material did not noticeably differ between these fractions. However, during leaching/extraction the slag particle size is an important parameter; the smaller particles react more rapidly and to a larger extent. On the other hand, small particles are more difficult to separate from the process solution prior to the carbonation step, while they also require more pre-processing in form of grinding or sieving, which increases energy consumption.

The kinetic modelling work discussed in Paper II is based on the assumption that reaction kinetics is governing the reaction rate. This assumption is valid for the small slag particle sizes (<250 μm) which were used in most of the experimental work. In case of larger slag particles the extraction rate becomes diffusion controlled. Table 3 lists the studied models based on the conversion rate of dissolving solid particles as a function of time. Functions 1-3 result in approximately linear time dependence with small slag particles, confirming the rate control by chemical kinetics. Correspondingly, functions 7-9 yield linear time relationships for large particles, thus showing the diffusion governance (Figure 3). For particles with an intermediate size of 250-500 μm both the kinetic and diffusion rate control functions give an approximately linear relationship.

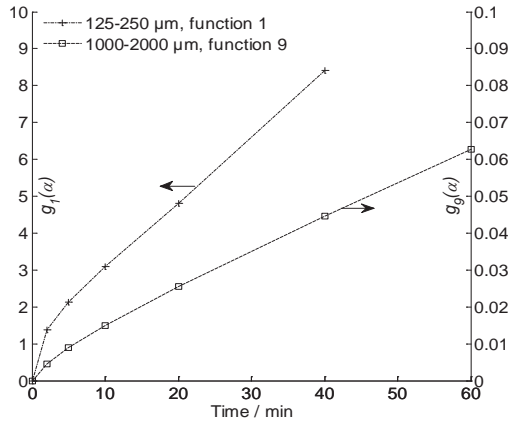


Figure 3. Time dependencies of functions $g_x(\alpha)$ for experiments 26 (125-250 μm slag particles, function 1 in Table 3) and 29 (1000-2000 μm slag particles, function 9 in Table 3). Data and experiment numbers from Paper II.

2.2. Slag-to-liquid ratio (Papers II-IV)

Slag-to-liquid mass ratio affects the calcium extraction efficiency, too. When ammonium salt solvent is present in over-stoichiometric amounts during extraction, a higher slag-to-liquid ratio increases the dissolution of impurities such as iron, magnesium and manganese. The increasing silicon extraction was especially found to reduce the maximum concentration of dissolved calcium. The effect of these trends is summarized in Figure 4 together with the effect of solvent concentration (Section 2.3.1). In addition, separation and handling of thicker (i.e. more dense and viscous) slurries can be more demanding from the processing point-of-view.

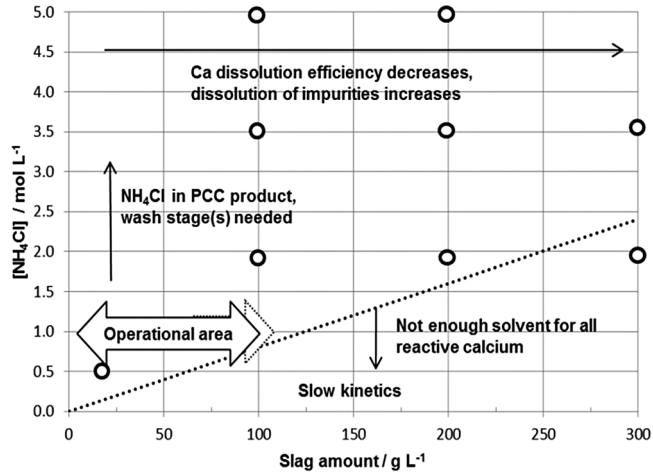


Figure 4. Observed limitations for selective calcium extraction with ammonium chloride solvent, the experiments listed in Paper IV are marked with circles.

2.3. Parameters steering PCC particle quality

Calcium carbonate has several crystal morphologies. The main polyforms are aragonite, calcite and vaterite, of which calcite is the most stable, while aragonite only forms at elevated temperatures, and the metastable vaterite rapidly transforms to calcite or aragonite. Figure 5 shows examples of these polyforms, as well as of the different crystal structures of calcite polymorph. In Figure 5 b) the calcite particles are of the so-called rhombohedral, cubical form, while the star-shaped particles in Figure 5 d) are scalenohedral.

In traditional PCC manufacturing, aragonite is the major polymorph at precipitation temperatures above 50 °C.¹⁶ Formation of vaterite and calcite at lower temperatures is controlled by the $[Ca^{2+}]/[CO_3^{2-}]$ ion ratio, an increase of $[Ca^{2+}]$ favouring the calcite form.^{13,14} Also, longer reaction time results in the transformation of vaterite to calcite. Normally, calcium is fed to the carbonation reactor as a calcium hydroxide ($Ca(OH)_2$) slurry, resulting in initial calcium concentration in precipitation varying between 0.001 and 0.04 mol/L.^{14,24}

Regarding the crystal structure of calcite, if the initial pH during precipitation is close to 13, the product will precipitate in scalenohedral form, while at lower pH values mainly rhombohedral crystals are formed.¹⁵ Longer reaction times yield larger particles, while rapid mass transfer of carbonate ions into the solution favours formation of small crystals. Earlier, this has been accomplished e.g. by introducing CO_2 to the reactor under high pressure (up to 90 bar)²⁵ or by feeding the CO_2 through frits with a small pore size to yield small gas bubbles.²⁶ At the same time, the $[Ca^{2+}]/[CO_3^{2-}]$ ion ratio should be maintained at the desired level.

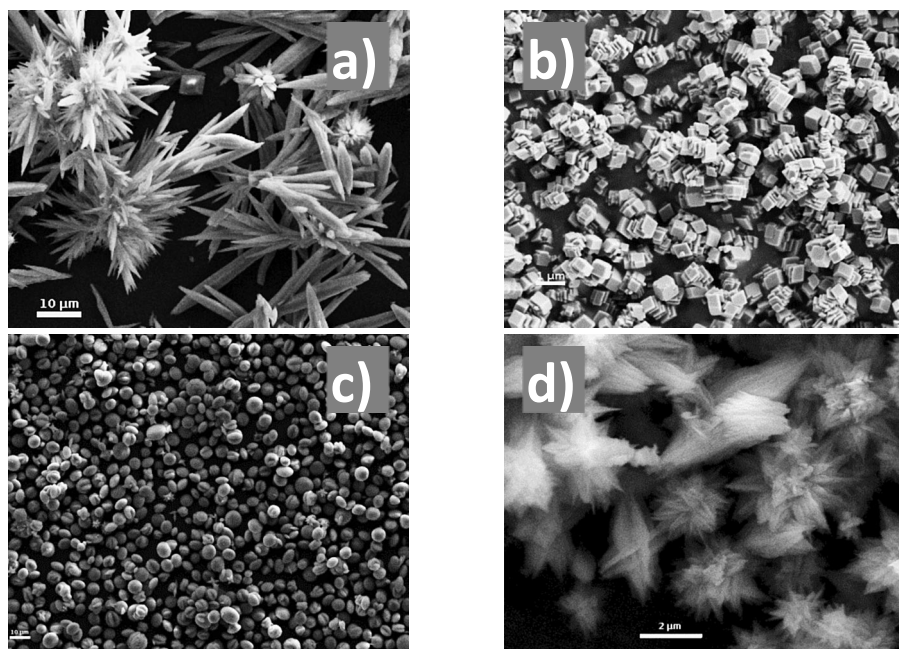


Figure 5. Scanning Electron Microscope (SEM) pictures of a) aragonite, b) rhombohedral calcite, c) vaterite and d) scalenohedral calcite particles produced with the Slag2PCC process. Scale bars 10 µm in a and c, 1 µm in b) and 2 µm in d).

The favoured PCC particle properties depend on the application. As an example, in papermaking the coated and uncoated paper qualities require different filler particles. Some types of fillers increase the mechanical strength, while others improve the optical properties. In general, the particle sizes of commercial products are below 2-3 µm, in special cases of nanometer scale.²⁷

Unlike in traditional PCC manufacturing, in the Slag2PCC process the particle morphology cannot be directly steered by controlling the supersaturation of the process solution with respect to calcium. This is caused by the slag being the calcium source; because only dissolved ions, not a slurry of $\text{Ca}(\text{OH})_2$, are transferred to the precipitation stage from extraction to ensure product purity, there is no excess undissolved calcium present during precipitation. The Slag2PCC technology nonetheless offers wide possibilities to control particle properties via e.g. calcium concentration and CO_2 gas flow rate, as discussed below.

2.3.1. Solvent concentration (Papers II-V)

The two-step Slag2PCC process can be operated according to several principles. If maximum utilization of steel slag is desired, it is essential to exceed the stoichiometric limitations defined by the Reactions R1 and R2 in Scheme 1; ammonium salt must be present in concentrations more than double the amount of reactive calcium in the slag. With higher solvent concentrations the calcium extraction occurs quicker, reducing the required reactor volumes. Too high levels (>1 mol/L) result in extraction of impurities

such as manganese and iron that miscolour the process solutions, but also of magnesium, vanadium, sodium and potassium (Figure 4). These elements accumulate in the process solutions, and may eventually precipitate together with the calcium carbonate, thus reducing the product purity.

In Table 4 the composition of three PCC samples produced with the Slag2PCC method is compared to four commercial PCC qualities. In general, the XRF analysis results are similar. Contents of elements such as iron and magnesium are even lower in the Slag2PCC process carbonates, but on the other hand sulphur and chlorine amounts can become higher than in commercial products.

Table 4. The chemical composition of various PCC samples produced with the Slag2PCC method (XRF analysis) compared to commercial qualities: 1) 0.50 mol/L NH_4Cl , 2) 0.65 mol/L NH_4Cl , 3) 1.84 mol/L NH_4Cl , 4) Schaefer Kalk GmbH & Co. KG PRECARB 100²⁸, 5) Schaefer Kalk GmbH & Co. KG PRECARB 150²⁹, 6) Minerals Technologies Inc. ALBACAR® 8101²⁷ 7) Minerals Technologies Inc. ALBAFIL®²⁷. The last column shows the weight loss by heating to 950°C. For entries labeled n.a. no information was available, for n.d. the element was not detected.

[%]	CaO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	MnO	P ₂ O ₅	S	Cl	950 °C
1	55.3	0.02	0.01	<0.01	<0.01	0.03	<0.01	0.03	<0.01	<0.01	0.08	n.d.	43.9
2	54.0	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.02	n.d.	44.4
3	53.3	0.02	<0.01	<0.01	0.02	0.03	<0.01	0.02	0.03	<0.01	0.04	2.8	44.3
4	55.5	0.04	n.a.	0.04	0.02	0.38	n.a.	n.a.	0.01	n.a.	0.01	n.a.	n.a.
5	55.5	0.04	n.a.	0.04	0.02	0.33	n.a.	n.a.	0.01	n.a.	0.02	n.a.	n.a.
6	54.9	n.a.	n.a.	n.a.	0.06	0.48	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
7	54.3	n.a.	n.a.	n.a.	<0.10	0.96	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

During the carbonation the over-stoichiometric solvent concentration approach causes high initial $[\text{Ca}^{2+}]$ values, even up to 0.25 mol/L depending on the chosen solid-to-liquid ratio and the reactive calcium content in the BOF slag. The initial carbonation pH remains low (at 9-10) compared to when using $\text{Ca}(\text{OH})_2$ in traditional PCC manufacturing (pH 12-13) because of the equilibrium between ammonium ions and ammonia present in the solution. Altogether, these conditions cause rapid growth and agglomeration of the formed CaCO_3 particles, yielding clusters with a diameter of 10-20 μm .

Alternatively, the initial carbonation solution pH can be increased by decreasing the ammonium salt solvent concentration. For example, in experimental work an initial NH_4Cl concentration of 0.01 mol/L during extraction resulted in a pH value of 12.6, and, based on stoichiometry, a dissolved calcium concentration of 0.005 mol/L prior to carbonation. Thus, the precipitation conditions resemble the traditional PCC production, yielding non-agglomerated particles with a diameter of 1 μm and smaller, but only a small fraction (<5 wt.-%) of the calcium present in steel slag is utilized during one extraction-carbonation cycle. In other words, complete conversion of

reactive calcium present in slag would require several extraction steps using the same slag, which increases the total processing time.

It is obvious that the operators of the Slag2PCC process must choose between efficient material processing and manufacturing of products with existing commercial markets.

2.3.2. CO₂ gas flow rate (Papers II-IV).

The gas flow into the carbonation reactor also affects the properties of the formed CaCO₃. At high flow rates (0.5 L_{gas}/(min*L_{liquid})) vaterite formation is preferred. Ten times smaller flow rates favour calcite precipitation, even though a short reaction time then still yields vaterite particles. As in traditional PCC production, a small bubble size is important for obtaining higher mass transfer rates and smaller particle sizes. During the experiments, frits with 10-50 µm pore size were used as gas inlets, yielding bubbles with diameters below 1.2 mm.

Theoretically, if pure CO₂ gas is used as a reactant, it is possible to choose such a small gas flow rate that the gas is completely absorbed by the process solution, making gas purging redundant. With flue gases containing only up to 30% CO₂, this approach is naturally not viable.

2.3.3. Temperature (Papers II-IV)

The extraction reaction occurs readily already at low temperatures; most of the experiments were performed at 20-30 °C, with residence times of 30-120 min. For the carbonate precipitation, the temperature is a more sensitive parameter. It controls the morphology of the calcium carbonate particles, as mentioned above. At temperatures above 50 °C the product will consist mainly of the aragonite polymorph instead of calcite. A higher temperature also increases the vapour pressure of ammonia, which thus becomes more volatile and eager to leave the process together with the non-reacted gases from the carbonation stage. If aragonite production with the Slag2PCC process is at some point desired, then this aspect is to be studied in more detail.

2.4. Reaction energies and exergies (Papers III, V)

Both the extraction and carbonation step reactions are exothermic, releasing energy to the surroundings as heat. Based on the modelling work discussed in Paper III, the cooling demand of the presented setup would be approximately 230 kW per one ton of processed slag to maintain a constant process temperature. This value is naturally subject to changes in slag reactivity and the process design itself, and the cooling can be realized with a separate heat exchanger or cooled reactor mantels of a suitable design or even by using cold make-up water. Because the process is preferably run at low, near ambient temperatures, the released energy can be utilized only to a limited extent as the exergy is low.

3. Operational and design features of the Slag2PCC process

Besides the parameters that arise directly from process chemistry via kinetics and thermodynamics as discussed in the previous section, the Slag2PCC process requires the design of several pieces of dedicated process equipment. The solutions presented below are based on the sub-demo scale (two 28 L reactors with separation equipment) process setup constructed by the author at Åbo Akademi University as a part of the research work (Paper IV; Figure 6). Additionally, an approximately ten times larger demo-scale setup (three 200 L reactors with separation equipment, Figure 7)³⁰ has been built for larger scale experiments by project partners at Aalto University, Espoo, Finland within the Cleen CCSP project (2011-2015).

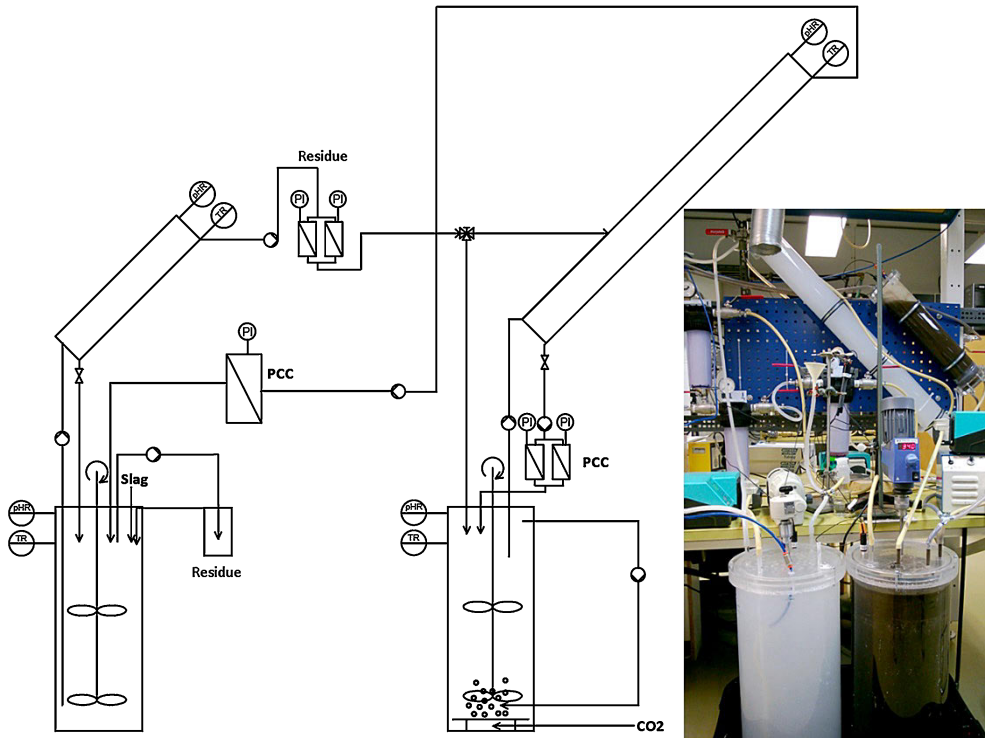


Figure 6. Process scheme and picture of the constructed demonstration setup at ÅAU.

3.1. Process operation principles

As discussed in Section 2.3, the Slag2PCC process can be operated in various ways. If the target is to produce large amounts of CaCO_3 , using BOF slag as efficiently as possible, continuous process operation offers the option to flexibly adjust parameters such as slag or CO_2 feed rates to maintain a nearly constant production rate, independently of changes in slag quality and composition. This option has been studied with process simulations (Aspen Plus) and with different scale experimental setups. (Papers III-IV; Figures 6 and 8) However, if the aim is to manufacture commercial quality PCC with well-defined crystal and particle properties, batch

carbonation meets this target by adapting the parameters currently used in the traditional PCC precipitation process. Also, different residence times required in the extraction and carbonation steps (Paper II) can be more easily implemented with a batch process. Both demo setup units are designed to be run in batch or continuous modes.

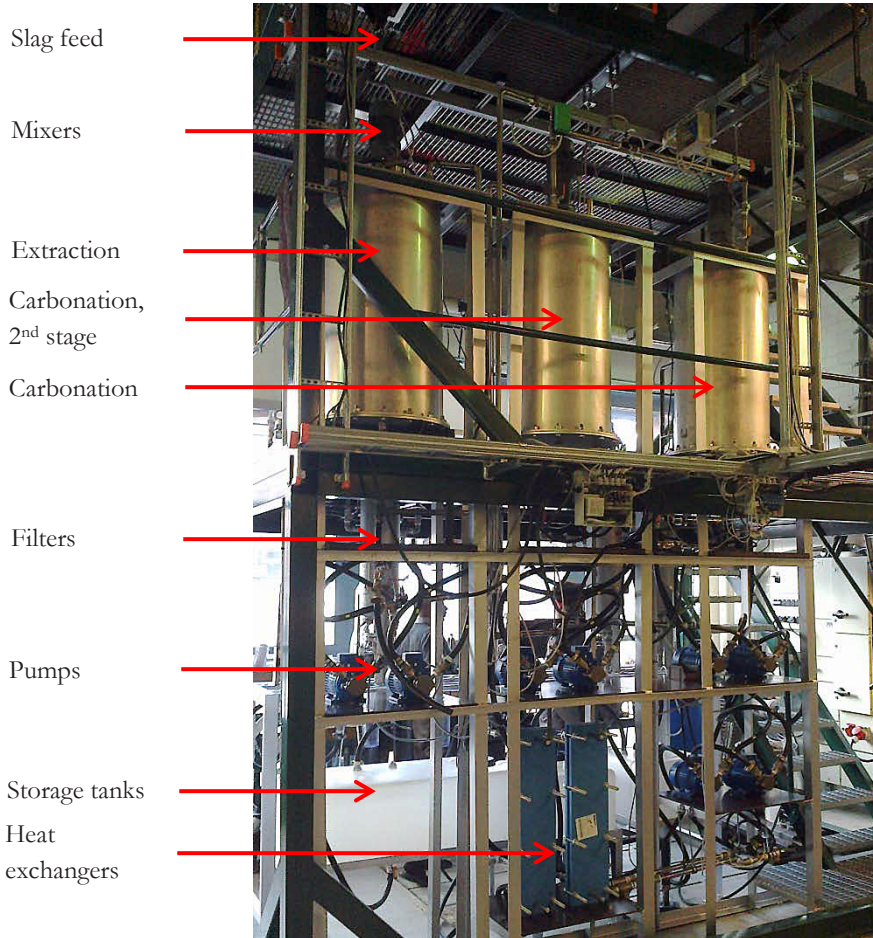


Figure 7. The demo-scale process setup at Aalto university, Espoo, Finland (March 2014).

3.2. Process control (*Paper IV*)

Reaction control of the Slag2PCC system is based on on-line pH and temperature measurements in the different reactors and other process units. These values enable both monitoring of the reaction extents and adjustment of the feed rates and other process parameters. Naturally, flow rates of the aqueous solutions and gas streams must be measured with calibrated flow meters, and level and pressure monitoring is required in the process units to guarantee safe system operation.

3.3. Process solution recycling (*Papers III-V*)

For the process economics, and because of environmental reasons, it is essential that the ammonium salt solution stays in the system and can be re-used. As an example, the allowed ammonium ion concentration in waste waters that are led to municipal treatment plants is low, 50 mg/L (2.8 mmol/L)³¹, compared to possible concentrations present in the Slag2PCC process. Losses of ammonium salt and water occur with the solids from both reaction steps while losses of ammonia and water vapour are possible with the gas purge from the carbonation stage, if this purge cannot be avoided.



Figure 8. The small-scale laboratory setup used for preliminary tests of continuous process operation and process solution recycling during autumn 2011. (Paper III)

If ammonium salt solvent is used in over-stoichiometric amounts as discussed in Section 2.3.1, washing of the solids is necessary for recovering the salt from the steel slag residue and from the produced PCC. At the same time, washing naturally also reduces the contamination of the PCC. From environmental point-of-view, this approach suffers from the washing water recycling and salt recovery, which is possibly the most energy-consuming step of the Slag2PCC technology, if accomplished by concentrating the solution by evaporating the water.³²

Alternative methods, such as membrane technologies, could possibly improve the efficiency and hence the economics of this process step, but the simplest option seems to be to use low concentration ammonium salt solvents. For instance, using 0.01 mol/L NH_4Cl solvent without washing the solids instead of 0.65 mol/L solvent with washing equipment, reduces the amount of required ammonium chloride make-up from 5.3 g/kg PCC to 1.1 g/kg PCC, while the energy-intensive washing water treatment is avoided. (Paper V)

A lower solvent concentration also decreases possible problems related to evaporation of the formed ammonia, a common issue in technologies using ammonia-based solutions for capture of gaseous emissions.^{33,34} Even though ammonia vapours can be captured e.g. in a scrubber or by active carbon filters, a simpler solution is to

limit ammonia formation in the system. In the case of an ammonia-containing flow of unreacted gases from the carbonation reactor must be purged, it could be sent through an HCl scrubber to capture ammonia and to simultaneously regenerate ammonium chloride. With this approach, however, it would be essential to ensure that the chloride ions are not accumulated in the process solutions.

Possible accumulation of dissolved ions (e.g. alkali) is also otherwise an important aspect to be studied further mainly as a part of experimental work with the larger demo setup at Aalto University. Because various elements dissolve from the slag during extraction, these may eventually precipitate with the produced calcium carbonate. On the other hand, addition of fresh make-up water to compensate for water losses dilutes the process solutions with respect to the minor elements and in the small scale experiments product contamination has remained on a low level (Table 4).

In addition, dissolved carbon dioxide, bicarbonate and carbonate ions present in the solution from the carbonator should preferably not enter the extraction reactor. The conditions with high calcium ion concentration will cause carbonate precipitation on slag particles, which reduces the extent of further extraction reactions, but also directly lowers the product yield from the carbonation stage. In the design of the demo setup units this is anticipated on by enabling some of the calcium-rich solution from extraction reactor to be used directly to increase the pH of the solution leaving the carbonation reactor. In absence of a CO₂ gas source, this results in precipitation of the dissolved carbon species and enables separation of these prior to the extractor.

The Aalto demo setup (Figure 7) has the necessary equipment to enable closed-system recycling of the solution between the reaction steps, which makes it possible to study these aspects in a more realistic way.³⁰

3.4. Mixing (Papers III-IV)

Traditional mechanical pitched paddle stirrers can be utilized for mixing the slurry of steel converter slag and the ammonium salt solution in the extraction reactor as well as the calcium-rich solution and the CO₂ gas bubbles in the carbonation step. For the sub-demo scale setup (Paper IV) the mixing energy dissipation is estimated at 0.35-0.50 W/kg of extraction solution. For the carbonation step this value was evaluated to be considerably lower, <0.1 W/kg solution, because of the three-phase mixture and smaller solids content present in the reactor. These values are based on solution viscosities calculated with a modified Einstein equation for non-Newtonian slurries (Paper III). Even though several variations of this equation exist in the literature^{35,36}, all of them result in similar values for the energy dissipation in the turbulent mixing conditions that are present in the reactors. At Aalto University, the installed electrical mixing power equals 1.7 W/kg for both reaction steps.³⁰

3.5. Separation of solid matter from the process solution (*Papers III-IV*)

Production of pure calcium carbonate requires efficient separation of solid slag particles after the extraction stage. For this purpose both inclined settlers^{37,38} and a hydrocyclone (Figure 9)³⁹ were tested in the sub-demo setup. Considering also the low space requirements compared to other types of e.g. gravitational thickeners or barrier filter units, both alternatives were found to give efficient pre-separation of solids, resulting in thickened slurry that in a larger scale process could be mechanically separated from the process solution. This staged separation reduces the load, cost and space requirements of traditional barrier filters, which are still necessary in the system as a second stage because of the small slag residue particles that are formed in the process. A Memtrex MMP921AAS membrane cartridge filter with 0.2 μm pore size was used for this purpose (Figure 9).

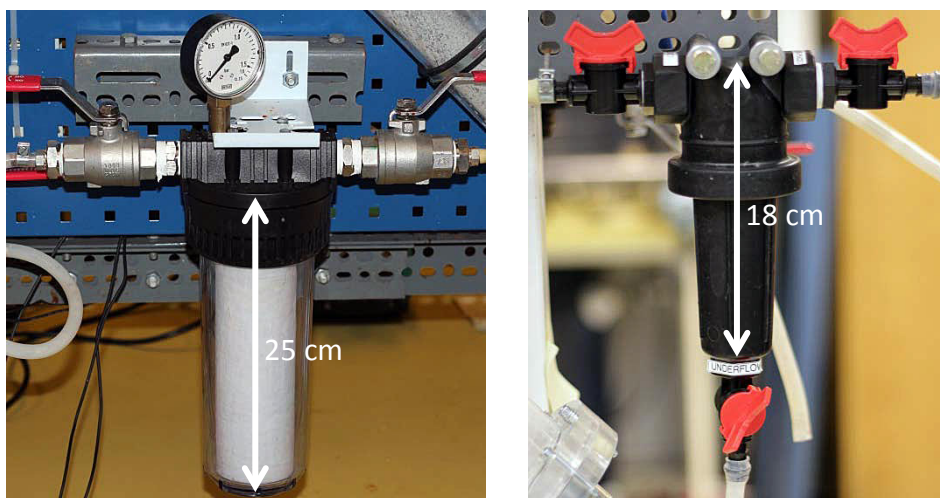


Figure 9. A cartridge filter unit with a pressure gauge for the 0.2 and 1.0 μm barrier filters (left) and a hydrocyclone³⁹ used in the experimental work (right).

The produced carbonate particles can, due to their micron-scale particle size, be effectively collected only with a suitable barrier filter. In the sub-demo setup the filter cartridges were of type AWP109-1, with 1 μm pore size (Figure 9). In traditional PCC manufacturing the product is dried with a filter press, which would be a good solution also for the solid products removed from the Slag2PCC process on larger scale, assuming that the final product is to be dried after washing. The Aalto demo unit uses 1 μm polypropylene bag filters combined with 0.4 μm membrane cartridge filters after each of the three reactors to separate all solid materials, both the slag and the produced PCC, from the liquid streams (Figure 7).³⁰

3.6. Material transport

The liquid process solution can be transferred between the reactors and separators using pumps. Because of the high solids content in the slurries, peristaltic pumps are a

good option for this purpose. At Aalto University the demo setup is equipped with pumps of 0.25 kW nominal power and maximum solution transfer rate of 20 L/min. Solid slag can be fed to the system with a Torex S.p.A RVR 02/10 screw feeder at a rate up to 20 L/min (Figure 7).³⁰ On an industrial scale the solid residue could also be removed from the process with screw transport equipment.

3.7. Reactor materials

Ammonium chloride solutions are corrosive at higher concentrations,²¹ and the ammonia which is formed during the extraction reaction can react with copper present in e.g. brass components. Thus the components that are in direct contact with the process solution should be manufactured of corrosion resistant materials such as stainless steel EN1.4521 (corrosion less than 0.1 mm/year).⁴⁰

3.8. Treatment of the slag residue

Because, as mentioned, at the highest 50 wt.-% of the calcium content is extracted from the BOF slag with the Slag2PCC process, and because the slag contains several inert elements and compounds, the amount of solid residue from the process is quite large. Based on experimental work, depending on the process conditions approximately 88 wt.-% of the slag mass fed to the process is returned as a residue. Various options for treatment of this material have been studied, from agricultural use to recovery of valuable metals such as vanadium, which are enriched during the calcium extraction stage. Research on this topic is ongoing primarily at Aalto University.

4. An alternative method for BOF slag carbonation

The Slag2PCC technology still has several challenges, as described in previous sections. From an economic point-of-view the main question is to find a commercial use for the produced carbonates. An alternative process for BOF slag carbonation has also been studied (Paper VI). The two-step process can be simplified by combining the extraction and carbonation steps into one reactor, as shown in Figure 10.

This process design generates two solid fractions; a carbonate rich, less dense fraction consisting of 60-75 wt-% of carbonates and a heavier fraction with approximately 10 wt-% of carbonate. Based on experimental work, these fractions can be separated by simple settling technologies. The carbonate-rich product has no value as a PCC-type filler, but it can possibly be re-used at the steel plant as a calcium source, thus reducing the need of other, natural calcium sources such as limestone.

Because in this process all the reactions in Scheme 1 would occur simultaneously in one reactor, continuously regenerating the solvent, the ammonium salt solution concentration could be much lower than the stoichiometric amounts possibly required in the two-step system. Moreover, during experiments the calcium extraction efficiency increased noticeably, up to 200% depending on the particle size, compared to the Slag2PCC concept. This was connected to the particle breakage effect caused by presence of carbon dioxide and the following carbonate formation in the slag particle pores.

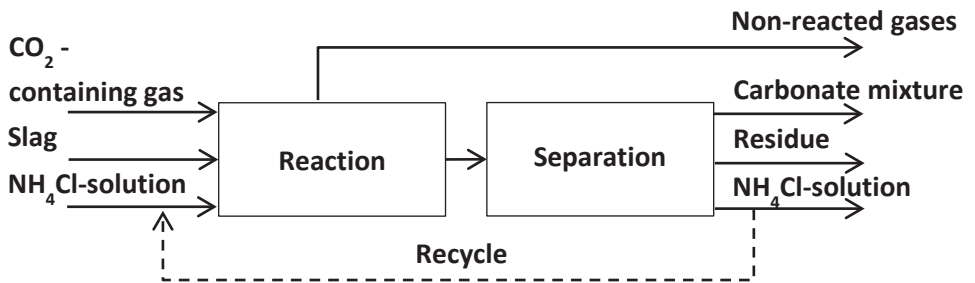


Figure 10. Process schema for one-step steel slag carbonation using gaseous carbon dioxide and an ammonium salt solution (Paper VI).

Aspects requiring further research for this technology are recyclability of the process solution and treatment of the slag residue. It should also be verified to which extent the carbonate product can be utilized in steelmaking. A clear advantage compared to the two-step process, however, is that the possible market would exist within the steel industry which produces waste slag and CO₂. Thus, the setup could be more readily integrated with existing processes.

5. Applicability and impacts of the Slag2PCC technology

The developed processes presented above have their limitations. Globally, the anthropogenic CO₂ emissions were 35 Gt/year in 2012, the estimated value for 2013 being 36 Gt/year.^{4,41} With respect to these huge numbers, the amount of steel slag available for carbonation is quite limited (Figure 1). Additionally, the suitability of the slags for this purpose varies, and the markets for the possible products are restricted. Rough estimation of the possible scale results in 20-30 Mt CO₂ captured/year depending on the slag reactivity, if all BOF slag produced worldwide would be utilized. On the other hand, global PCC markets were only 14 Mt in 2011, which shows that if the carbonation processes are to be used in large scale, some of the produced carbonates must be used for other applications besides PCC. (Papers I, IV, V)

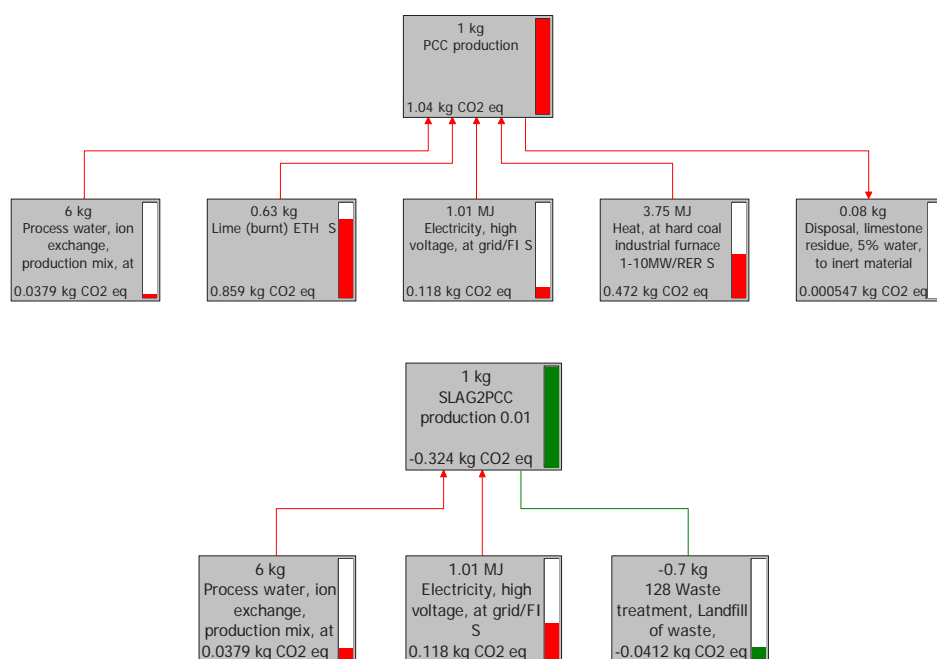


Figure 11. Contribution of the sub-processes on the carbon dioxide balance of the traditional PCC production process (up) and the Slag2PCC processes with 0.01 M NH₄Cl solvent (down). Impact reductions are shown in green and sub-processes with impact < 4% are hidden for clarity in case of the 0.01 M Slag2PCC (Paper V).

However, these carbonation processes could serve as demonstration of CO₂ mineralization technologies. Compared to other related approaches using more vast resources such as magnesium-rich minerals,⁴² the here discussed processes have the advantage of existing markets for the manufactured products. Thus, there exists a possible financial incentive of using the developed technologies, even though the price of carbon dioxide emissions is currently very low, only 6 €/ton emitted.⁴³

From an environmental point of view, the Slag2PCC process would be viable, having a small or even a negative environmental impact footprint, depending on the calculation method, as shown by the LCA studies discussed in Paper V. Comparing e.g. the carbon dioxide emissions from traditional PCC manufacturing and a low solvent molarity Slag2PCC process (Figure 11) it is found that while production of 1 kg PCC from natural resources generates 1.04 kg CO₂ equivalents, the Slag2PCC process binds 0.32 kg CO₂. In other words, if traditional production is replaced by the alternative technology, the avoided carbon dioxide emissions can be estimated in total to equal 1.36 kg CO₂ equivalents. At the same time, the amount of landfilled waste slag and use of natural resources would be reduced.

As mentioned in Section 3.3 and in Paper V, high solvent molarities in the Slag2PCC process could actually result in larger emissions compared to the traditional process, which shows that it is essential to consider all the process steps in the feasibility studies.

6. Conclusions and future work

In this thesis it is shown that methods for utilisation of solid industrial waste materials, more specifically steel converter or basic oxygen furnace (BOF) slags for production of calcium carbonate via scientifically novel process routes are able to reduce consumption of natural resources such as limestone. At the same time they can, if optimized as complete processes, reduce the anthropogenic CO₂ emissions by capturing carbon dioxide, even though the captured amounts are significant only in scale of individual industrial plants, not globally. From the scientific point-of-view, the technologies would serve as demonstrations of the mineral carbonation processes possessing a larger CO₂ storage potential. Depending on the process, the produced carbonates could find use for instance in papermaking as a filler material or in steelmaking as a fluxing agent.

However, as a part of the on-going (2011-2015) CCSP project, it is essential to confirm that the commercial PCC in e.g. papermaking industry can be replaced by the Slag2PCC products. The critical aspects still demanding attention are especially the particle size and morphology of the produced carbonates, while the already obtained level of sufficient product purity shall be maintained, too. The PCC produced with the demo setup at Aalto University may be used to manufacture test paper sheets in the laboratory to study the practical properties of the filler material. As mentioned, the demo setup can also be used to verify the lifetime of the process solvent solutions in a more realistic way compared to lab-scale experiments. The formed slag residue can, after possible separation of valuable metals, be tested for use as e.g. construction aggregates.

The largest challenges prior to implementation of the developed technologies into industrial scale are, however, not scientific or technical. Especially, because the Slag2PCC process would connect steel and papermaking industries in a way which so far has not existed, using the technology would require a new type of co-operation from the various companies. The developed one-step calcium carbonate production method could be implemented within the steel plant, making the concept more readily applicable even though it still requires further studies especially on the product quality.

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