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REDUCTION OF CO_2 EMISSIONS BY MINERAL CARBONATION: STEELMAKING SLAGS AS RAW MATERIAL WITH A PURE CALCIUM CARBONATE END PRODUCT

Doctoral Dissertation

Sanni Eloneva

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Faculty of Engineering and Architecture
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Abstract

Mineral carbonation is one of the options that can contribute to the reduction of carbon dioxide emissions for climate change mitigation purposes. Steel manufacturing, which is one of the biggest industrial sources of CO_2 emissions, could benefit from this option by utilizing its own by-products, i.e., steelmaking slags, to combine with CO_2. Additional benefits would be achieved if the end product was a pure and marketable calcium carbonate. The utilization of $CaCO_3$ derived from steelmaking slag to replace some of the synthetic $CaCO_3$ used in industry would simultaneously save virgin material resources, reduce carbon dioxide emissions, and provide a new utilization option for the low-value slag.

The objective of the research reported in this thesis was to investigate the possibility of reducing CO_2 emissions by utilizing steelmaking slags as raw material for CO_2 mineralization. The target was that the end product of the CO_2 mineralization would be a pure $CaCO_3$ suitable for utilization. The suitability of the acetic acid process route suggested by Kakizawa et al. (2001) was tested first. Experiments showed that acetic acid dissolves calcium efficiently from steelmaking slags. A weak acetic acid solution was able to dissolve lime selectively from the steel converter slag, forming a clearly alkaline solution. Nonetheless, efficient $CaCO_3$ precipitation required the addition of NaOH to prevent the regeneration of acid during carbonation, as well as to increase the alkalinity of the solution in those cases where a stronger acetic acid solution was used for the dissolution step. Preliminary process calculations revealed that chemical costs make the process clearly too expensive for CO_2 sequestration.

Because the production of pure $CaCO_3$ from steelmaking slags with acetic acid was not feasible, various other solvents were tested. Three ammonium salt solutions (CH_3COONH_4, NH_4NO_3, and NH_4Cl) dissolved calcium selectively from the steel converter slag and almost as efficiently as acids. The precipitated calcium carbonates were very pure. It was calculated that the production of pure calcium carbonate from steel converter slag by using ammonium salts as a solvent has clearly negative CO_2 emissions. Since it was found that the method is not suitable for just any waste/by product materials that contain calcium, but should be applicable for at least those that contain free CaO, this method has potential only for minor-scale, yet significant, CO_2 storage. A clear advantage is, however, that it uses a low value by-product as its raw material and has economic potential.

Keywords mineral carbonation, steelmaking slag, calcium carbonate, acetic acid, ammonium salt

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Väitöskirjan nimi
Hiilidioksidipäästöjen vähentäminen mineraalien karbonoinnilla: teräksentuotannon kuonat raaka-aineena ja puhdas kalsiumkarbonaatti lopputuotteena

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Työn valvoja Carl-Johan Fogelholm, Prof.
Työn ohjaaja Ron Zevenhoven, Prof. ja Sebastian Teir, TkT

Tiivistelmä

Mineraalien karbonointi on yksi menetelmistä, jota voidaan käyttää hiilidioksidipäästöjen vähentämiseen ilmastonmuutoksen hillitsemiseksi. Teräksentuotanto, joka on yksi suurimmista teollisista CO_2-lähteistä, voisi hyötyä tästä menetelmästä käyttämällä omaa sivutuotettaan, eli teräksentuotannon kuonaa, sitomaan CO_2:a. Lisäetua saavutetaan, jos lopputuote olisi puhdasta ja myytäväksi kelpaavaa $CaCO_3$:a. Käyttämällä teräksentuotannon kuonista tuotettua $CaCO_3$:a korvaamaan teollisuudessa käytettävää synteettistä $CaCO_3$:a säästettäisiin samanaikaisesti neitseellisiä luonnonvaroja, vähennettäisiin CO_2-päästöjä sekä tarjottaisiin uusi käyttömahdollisuus edulliselle kuonalle.

Tämän työn tavoitteena oli tutkia mahdollisutta vähentää CO_2-päästöjä käyttämällä teräksentuotannon kuonia raaka-aineena CO_2:n mineralisoimiseen. Tämän CO_2:n mineralisoimisen lopputuotteena tuli olla puhdasta hyödynnettävissä olevaa $CaCO_3$:a. Ensimmäiseksi tutkittiin Kakizawan ym. (2001) ehdottaman etikkahappoprosessin soveltuvuutta. Kokeet osoittivat, että etikkahappo liuottaa kalsiumia teräksentuotannon kuonista tehokkaasti. Laimea etikkahappoliuos kykeni liuottamaan kalsiumoksidia selektiivisesti teräskonvertterikuonasta, muodostaen selvästi emäksisen liuoksen. Tehokas $CaCO_3$:n saostaminen vaati kuitenkin NaOH:n lisäämistä estämään hapon regeneroitumista sekä lisäämään liuoksen emäksisyyttä niissä tapauksissa jolloin liuotusvaiheessa käytettiin vahvempaa etikkahappoliuosta. Alustavien prosessilaskelmien mukaan kemikaalien käytöstä johtuvat kustannukset tekevät prosessista liian kalliin CO_2:n talteenotolle.

Koska $CaCO_3$:n tuottaminen teräksentuotannon kuonista etikkahapon avulla ei ollut kannattavaa, useita muita liuoksia testattiin. Kolme ammoniumsuolaliuosta (CH_3COONH_4, NH_4NO_3 ja NH_4Cl) liuottivat kalsiumia teräskonvertterikuonasta selektiivisesti ja lähes yhtä tehokkaasti kuin hapot. Saostuneet kalsiumkarbonaatit olivat hyvin puhtaita. Laskelmien perusteella teräskonvertterikuonasta ammoniumsuolaliuoksia käyttämällä tuotetun puhtaan kalsiumkarbonaatin tuotannolla on selvästi negatiiviset CO_2-päästöt. Menetelmä ei sovellu mille tahansa kalsiumpitoiselle jäte-/sivutuotemateriaalille, mutta sen pitäisi soveltua ainakin niille jotka sisältävät vapaata kalkkia, joten sillä on potentiaalia vain pienen, mutta kuitenkin merkittävän, skaalan CO_2:n varastoinnille. Selkeä etu on kuitenkin se, että siinä käytetään edullista sivutuotetta raaka-aineena ja sillä on taloudellista potentiaalia.

Asiasanat mineraalien karbonointi, teräksentuotannon kuonat, kalsiumkarbonaatti, etikkahappo, ammoniumsuola

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Preface

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learn. I wish to thank my brother, Tuomo, for ensuring that my life has never been too easy and for making me laugh. Finally, I want to thank my dear husband, Antti, for his love and friendship, as well as for keeping my life in balance and for believing in me.

Sanni Eloneva

Kaukauna, October 2010

Contents

List of Publications

This thesis consists of an overview and of the following papers.

I Teir S., Eloneva S., Fogelholm C-J., Zevenhoven R., 2007. Dissolution of Steelmaking Slags in Acetic Acid for Precipitated Calcium Carbonate Production. Energy; 32 (4): 528-539.

II Eloneva S., Teir S., Salminen J., Fogelholm C.-J., Zevenhoven R., 2008. Fixation of CO_2 by carbonating calcium derived from blast furnace slag. Energy; 33 (9): 1461-1467.

III Eloneva S., Teir S., Salminen J., Fogelholm C-J., Zevenhoven R., 2008. Steel converter slag as a raw material for precipitation of pure calcium carbonate. Industrial & Engineering Chemistry Research; 47 (18): 7104-7111.

IV Eloneva S., Teir S., Revitzer H., Salminen J., Said A., Fogelholm C.-J., Zevenhoven, R., 2009. Reduction of CO_2 emissions from steel plants by using steelmaking slags for production of marketable calcium carbonate. Steel Research International; 80 (6): 415-421.

V Eloneva S., Said A., Fogelholm C.-J., Zevenhoven R., 2010. Feasibility Study of a Method Utilizing Carbon Dioxide and Steelmaking Slags to Produce Precipitated Calcium Carbonate (PCC). In Proceedings of International Conference on Applied Energy (ICAE), Singapore, April 21-23: 169-178.

VI Eloneva S., Puheloinen E.-M., Kanerva J., Ekroos A., Zevenhoven R., Fogelholm C.-J., 2010. Co-utilisation of CO_2 and steelmaking slags for production of pure $CaCO_3$ – legislative issues. Journal of Cleaner Production; 18 (18): 1833-1839.

Author's contribution

I Sanni Eloneva planned and carried out the experiments, as well as the interpretation of the results, in collaboration with Sebastian Teir. Sanni Eloneva also assisted Sebastian Teir in writing the article.

II Sanni Eloneva planned and carried out the experiments in collaboration with Sebastian Teir. The author also carried out most of the interpretation of the results and performed all the thermodynamic calculations. Sanni Eloneva wrote most of the paper as well.

III Sanni Eloneva planned the experiments in collaboration with Sebastian Teir. Sanni Eloneva carried out the experiments and was responsible for the interpretation of the results and for writing most of the paper.

IV Sanni Eloneva planned the experiments in collaboration with the co-authors and was responsible for the interpretation of the results, performing the thermodynamic calculations, and writing the paper.

V Sanni Eloneva was responsible for planning the experiments, carrying out part of the experiments, the interpretation of the results, the process evaluation, and for writing the paper.

VI Sanni Eloneva was responsible for planning the experiments, the interpretation of the experimental results, and for writing most of the paper.

Nomenclature

Abbreviations

AAS	Atomic absorption spectrometry
APC	Air Pollution Control
ARC	Albany Research Center
CCS	Carbon (dioxide) capture and storage
FB	Fluidized bed
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
MSWI	Municipal solid waste incineration
PCC	Precipitated calcium carbonate
SEM	Scanning Electron Microscope
TC	Total Carbon
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy

Symbols

W	Work	[kWh/t]
W_i	Work index of the slag	[kWh/t]
W_{P80}	Passing size of the product (slag)	
W_{F80}	Passing size of the feed (slag)	

Chemical compounds and minerals

Al_2O_3	Aluminum oxide

$AlO(OH)$	Aluminum oxide hydroxide
$Al(NO_3)_3$	Aluminum nitrate
$Al_2(SO_4)_3$	Aluminum sulphate
$Al_2O_3 \cdot H_2O$	Bohmite
CH_3COOH	Acetic acid
$Ca_2(Mg_{0.5}Al_{0.5})(Si_{1.5}Al_{0.5}O_7)$	Akermanite-gehlenite
$Ca_3Al_{0.84}Fe_{1.16}Si_3O_{12}$	Andradite aluminian
CH_3COONH_4	Ammonium acetate
Ca_2FeAlO_5	Brownmillerite
$Ca(CH_3COO)_2$	Calcium acetate
$Ca_2Fe_2O_5$	Calcium iron oxide; srebrodolskite
$CaCO_3$	Calcium carbonate
$CaCl_2$	Calcium chloride
$Ca(OH)_2$	Calcium hydroxide; slaked lime, milk of lime
CaO	Calcium oxide; lime
CO_2	Carbon dioxide
Cr_2O_3	Chromium oxide
$Ca_2(Al(AlSi)O_7)$	Gehlenite
Ca_2SiO_4	Larnite
$Ca_3Mg(SiO_4)_2$	Merwinite
$CaMgSiO_4$	Monticelite
CaS	Oldhamite
CH_3CH_2COOH	Propionic acid

CH_3COONa	Sodium acetate
$CaSiO_3$	Wollastonite
EDTA	Ethylenediaminetetraacetic acid
FeO	Iron oxide; wuestite
Fe_3O_4	Magnetite
HCl	Hydrochloric acid
H_4SiO_4	Monosilicic acid
HNO_3	Nitric acid
H_2SO_4	Sulphuric acid
H_2O	Water
K_2O	Potassium oxide
$MgCO_3$	Magnesium carbonate; magnesite
$Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$	Magnesium carbonate; hydromagnesite
$MgCO_3 \cdot 3H_2O$	Magnesium carbonate trihydrate; nesquehonite
$MgCl_2$	Magnesium chloride
$MgCl_2 \cdot 6H_2O$	Magnesium chloride hexahydrate
$MgCl_2(H_2O)_n$	Magnesium chloride hydrate; molten salt
$Mg(OH)_2$	Magnesium hydroxide
$Mg(OH)Cl$	Magnesium hydroxide chloride
$Mg(NO_3)_2 \cdot 6H_2O$	Magnesium nitrate hexahydrate
MgO	Magnesium oxide
$MgSO_4$	Magnesium sulphate
MnO_2	Manganese dioxide

$(Mg, Fe)_2SiO_4$	Olivine
$Mg_3Si_2O_5(OH)_4$	Serpentine
NH_3	Ammonia
$(NH_4)_2CO_3$	Ammonium carbonate
NH_4Cl	Ammonium chloride
$NH_4H_2PO_4$	Ammonium di-hydrogen phosphate
NH_4OH	Ammonium hydroxide
NH_4NO_3	Ammonium nitrate
$(NH_4)_2SO_4$	Ammonium sulphate
$(NH_4)_2HPO_4$	Diammonium hydrogen phosphate
$Na_2Mg(CO_3)_2$	Double carbonate eitelite
NO_3	Nitrate
NO_2	Nitrogen dioxide
$NaCa_2Si_3O_8(OH)$	Pectolite
$NaHCO_3$	Sodium bicarbonate
$NaCaSiO_3(OH)$	Sodium calcium hydroxysilicate
Na_2CO_3	Sodium carbonate
$NaCl$	Sodium chloride
$NaOH$	Sodium hydroxide; caustic soda
$NaNO_3$	Sodium nitrate
Na_2O	Sodium oxide
$(NH_2)_2CO$	Urea
PO_4	Phosphate

SiO_2	Silicon dioxide; silica, quartz
SO_4	Sulphate
SO_2	Sulphur dioxide
TiO_2	Titanium oxide
V_2O_3	Vanadium oxide

List of Figures

List of Tables

1 Introduction

1.1 Climate change mitigation

Concern over climate change and its possible effects has risen slowly but steadily during the past few decades. It has been widely accepted that climate change is already occurring and its progress should be mitigated so that negative effects are minimized. Since carbon dioxide (CO_2) is the most significant anthropogenic greenhouse gas (IPCC, 2007), its reduction is necessary for climate change mitigation. Most of these emissions come from fossil fuel use, and thus the main strategies to reduce these emissions include the replacement of fossil fuel-based energy by renewable energy or nuclear power, the reduction of energy consumption by, for instance, increasing energy efficiency, and carbon dioxide capture and storage (CCS). The replacement of fossil fuels by renewable energy or nuclear power is definitely not an easy task, since most of the energy supply today is covered by fossil fuels (IEA, 2007). Nuclear power is also opposed because of the safety risks and as yet unsolved problems with the nuclear waste related to it. The reduction of energy consumption is very difficult, maybe even impossible, since the increase in economic growth is closely related to an increase in energy consumption (Shell International, 2001). By increasing energy efficiency, the increase in energy consumption could be slowed down. Carbon dioxide capture and storage (i.e., CO_2 sequestration), in which carbon dioxide is captured from its source and then stored permanently, would allow the continued use of fossil fuel combustion while reducing the atmospheric carbon dioxide emissions. It is unlikely that any of these methods alone could solve the problem, and thus a combination of methods is needed.

1.2 Steelmaking slags and mineral carbonation

The steel industry is one of the biggest sources of industrial CO_2 emissions, accounting for about 7% of the total anthropogenic CO_2 emissions to the atmosphere (Kim and Worrell, 2002). The reduction of these emissions for climate change mitigation will not be easy, because the industry is heavily dependent on either electricity or coal. Most steel is produced either via the integrated process route or via the electric arc furnace route. In the integrated process route coal is used as one of the main raw materials to produce molten iron, which is used to manufacture steel. In the electric arc furnace route electricity is used to melt recycled steel into the end product. A large part of the world's electricity generation is based on fossil fuels, producing substantial amounts of CO_2. However, steel manufacturing has an interesting by-product, steelmaking slag, which could probably be used to reduce part of its CO_2 emissions. Steelmaking slags have a high calcium oxide content, which makes them likely to be suitable for use as raw material in mineral carbonation, one method for carbon dioxide sequestration.

Mineral carbonation (i.e., carbon dioxide mineralization) is a method in which magnesium oxides or calcium oxides in silicate minerals are promoted to react with carbon dioxide to form carbonates:

$$
\begin{aligned}
&(Mg,Ca)_x Si_y O_{x+2y} \cdot zH_2O(s) + xCO_2(g) \\
&\qquad \rightarrow x(Mg,Ca)CO_3(s) + ySiO_2(s) + zH_2O(l)
\end{aligned}
\tag{1}
$$

One clear advantage compared to other carbon dioxide storage methods is that the product of carbon dioxide mineralization, magnesium carbonate or calcium carbonate, is thermodynamically stable under ambient conditions (Newall et al., 2000). Thus this method could store carbon dioxide for a very long time (Lackner, 2003), making post-storage monitoring of carbon dioxide stored as carbonates unnecessary. Currently, the main disadvantage of mineral carbonation is that although the net carbonation reaction is exothermic (Equation 1), large amounts of additives and/or energy are needed to speed up the slow reaction.

Estimations of the world's annual steelmaking slag production vary between 220 and 420 Mt (USGS, 2006). With a calcium oxide content of 34-52% (U.S. Department of Transportation, 1998), ideally, this amount could store up to 170 Mt of carbon dioxide per year by mineral carbonation. While the CO_2 fixation capacity of natural silicate minerals is far greater than that (Lackner, 2003), steelmaking slags are appealing because they are readily available, removing the need to mine and transport huge amounts of minerals.

1.3 Precipitated calcium carbonate

As a result of the high calcium content of steelmaking slag, the carbonate product would consist mostly of calcium carbonate. This calcium carbonate could probably be used to replace some of the limestone used within industry, and, if it met the high standards of synthetic calcium carbonates, it could probably be sold at a high price. Natural calcium carbonate (i.e., limestone) is used for various purposes, such as manufacturing concrete or Portland cement, and producing lime to be used in, for example, soil stabilization and neutralization, glassmaking, water treatment, and flue gas desulphurization (Harben and Kuzvart, 1997). Synthetic calcium carbonate, a.k.a. precipitated calcium carbonate (PCC), is used as a filler and coating pigment in plastics, rubbers, paints, and papers. It is consumed mainly by the paper industry and has quite a high price (>€100/t) (Nordkalk Oy, 2004). Its total annual consumption is approximately 13 Mt worldwide, of which roughly 0.5 Mt is produced in Finland (Roskill, 2008).

The advantage of PCC over limestone is that in its production process impurities can be removed from the limestone and the properties of the produced calcium carbonate can be controlled. The $CaCO_3$ content of PCC is generally higher and the SiO_2 and MgO contents are lower than those of limestone (Roskill, 2008). The utilization of steelmaking slags to replace limestone in PCC manufacturing would simultaneously save virgin material resources, reduce carbon dioxide emissions, and provide a new utilization option for the low-value slag.

Steelmaking slags contain other compounds and elements besides calcium oxide. Therefore, the production of marketable calcium carbonate from steelmaking slags would probably require a process in which calcium is separated from the slag prior to carbonation; otherwise, the carbonate product would contain some of the silicon and other elements of the raw material.

1.4 Outline of this thesis

The objective of the research reported in this thesis was to investigate the possibility of reducing CO_2 emissions by utilizing steelmaking slags as raw material for CO_2 mineralization. The target was that the end product of the CO_2 mineralization would be a pure calcium carbonate suitable for utilization. The advantages gained from this option would be reduced CO_2 emissions, the saving of virgin material resources, and the creation of a new utilization option for the low-value slag.

The literature relevant to this work is reviewed in Chapter 2, followed by the objective of the research presented in this thesis in Chapter 3. The work in Publications I to VI is aggregated in Chapters 4 and 5, and the conclusions are summarized with recommendations for future work in Chapter 6.

2 Literature review

2.1 Mineral carbonation

2.1.1 History

Mineral carbonation is based on the idea that carbon dioxide is fixed with metal oxide-bearing minerals, forming a stable carbonate as an end product. In nature, atmospheric CO_2 forms carbonic acid with water and this acid reacts with alkaline rocks, forming insoluble carbonates and thus storing CO_2 (IPCC, 2005). However, this so-called rock weathering takes place on geological timescales and is thus too slow for mitigating human-induced climate change. In 1990, Seifritz (1990) suggested copying this natural phenomenon for a process that would reduce carbon dioxide emissions. Dunsmore (1992) proposed the use of calcium-rich brines for locking up CO_2 as calcium carbonate. The first comprehensive mineral carbonation research was reported by Lackner et al. (1995) in 1995 and since then research has continued in various different laboratories or research groups around the world.

2.1.2 Suitable raw materials

Calcium and magnesium oxides or hydroxides would be ideal materials for storing CO_2 as carbonate minerals (Lackner et al., 1995; IPCC, 2005). However, these are too rare in nature for any large-scale CO_2 sequestration. Minerals that contain calcium or magnesium but do not contain carbonate, such as magnesium and calcium silicates, on the other hand, seem to have potential. Carbonate-containing materials (such as limestone) cannot be used for mineral carbonation as they have already been carbonated and thus have no capacity to fix more CO_2. Carbonates formed from the alkali metals (such as Na or K) are too soluble in water and thus these are not suitable either. Other alkaline-earth metal-bearing minerals are too rare and, while iron-bearing minerals could in theory be used for carbonation, these are likely to be too valuable a commodity for large-scale mineral carbonation purposes.

Magnesium and calcium silicates can be found from ultramafic and mafic rocks (Huijgen and Comans, 2003; IPCC, 2005). In these rocks magnesium silicates exist in the form of dunites, peridotites, and serpentinites, for example. Dunite consists mainly of a magnesium iron silicate called olivine ($(Mg, Fe)_2SiO_4$), peridotite consists of olivine and pyroxene, and serpentinite is composed of the serpentine group minerals, such as serpentine ($Mg_3Si_2O_5(OH)_4$). Since magnesium silicates are available in abundant amounts, the theoretical carbon dioxide storage capacity potential of mineral carbonation is estimated to exceed all the possible fossil carbon-based carbon dioxide emissions ever generated on earth (Lackner, 2003; Lackner et al., 1995; IPCC, 2005). Rocks containing calcium silicates, for example basalts and wollastonite ($CaSiO_3$), have a clearly lower CO_2 storage potential, as they either have a low calcium content (basalts) or are quite rare in nature (wollastonite) (Lackner et al., 1995; IPCC, 2005).

In addition to the large CO_2 storage capacity of magnesium silicates, their clear advantage is that reserves of them are present in all continents, although not necessarily in all countries (IPCC, 2005). However, for a country like Finland, where no suitable geological storage locations exist, but which has large magnesium silicate deposits (Teir et al., 2006), mineral carbonation offers a significant domestic CO_2 storage option. What is especially interesting is that huge amounts of these minerals have already been mined simultaneously with industrial minerals and metals.

On the basis of the magnesium or calcium contents of the silicates, the amount of rock required for storing CO_2 is from 2 to 7 times the amount of CO_2 fixed (Lackner, 1995). This would lead to significant mining operations, although it is argued that more material is moved and a larger area is disturbed by mining the coal that generates the CO_2 that would be treated by these minerals (IPCC, 2005).

While natural calcium and magnesium silicates clearly hold the largest CO_2 storage capacity, industrial waste and by-product materials, such as steelmaking slags, ashes from power plants and municipal solid waste incinerators, de-inking ash from paper recycling, and waste concrete (Huijgen and Comans, 2005; Johnson, 2000; Uibu et al., 2009; Iizuka et al., 2004), are tempting raw materials for mineral carbonation as they are readily available and typically close to a significant CO_2 source. These also tend to be more reactive than natural minerals (e.g., Teir, 2008).

2.1.3 Proposed mineral carbonation methods

Currently, mineral carbonation research is mainly at the level of laboratory-scale research. The mineral carbonation process concepts that have been studied can roughly be divided into direct and indirect methods. In direct methods, the mineral is carbonated in one step, while in indirect methods, the reactive element (such as Ca or Mg, as ions or oxides, hydroxides,…) is first extracted from the mineral prior to carbonation (Figure 1). The end product of indirect mineral carbonation is usually quite a pure carbonate. In situ mineral carbonation, i.e., geological storage of CO_2 in carbonate form, is outside the scope of this work and, therefore, is not included.

Various pre-treatment methods, such as grinding, heat activation, magnetic separation, and surface activation, have been suggested in order to speed up the carbonation rate. Unfortunately, none of these methods has yet proven to be energy-efficient and effective at the same time, although the CO_2 emissions from producing the power needed for conventional grinding are typically small and might be considered tolerable. These methods have been reviewed in more detail by Huijgen (2007).

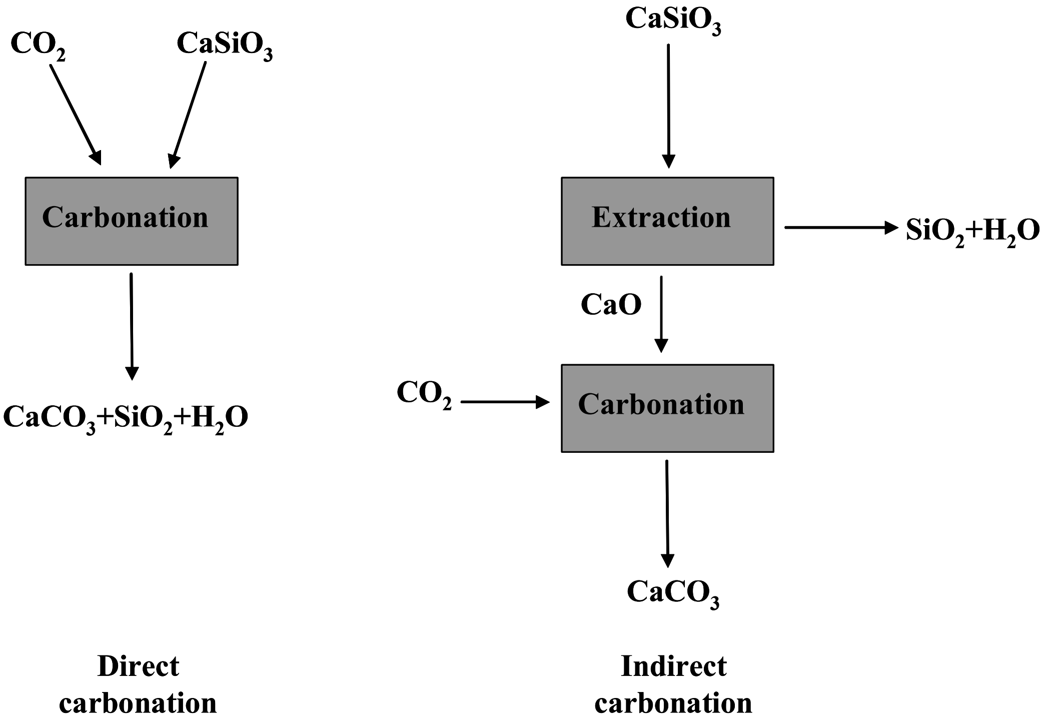

Figure 1. Basic principles of the direct and indirect carbonation methods (wollastonite ($CaSiO_3$) is used as an example) (Eloneva, 2008).

Maybe the most energy-efficient process route proposed in the literature is the *direct gas-solid process*, because it would allow for the simultaneous production of high-temperature heat and reduction of carbon dioxide emissions. In theory, this process route is very straightforward: a mineral silicate is exposed to carbon dioxide gas, forming carbonate, silicon dioxide, and water (the reaction for serpentine is presented in Equation 2).

$$Mg_3Si_2O_5(OH)_4(s) + 3CO_2(g) \rightarrow 3MgCO_3(s) + 2SiO_2(s) + 2H_2O(g) \qquad (2)$$

At high temperatures (below calcination temperature) and low pressure the conversion was found to be insignificant (Lackner, 1997). Higher pressures allow higher temperatures to be used and should therefore increase reaction speed. With serpentine, 30% conversion has been reached at a pressure of 340 bar. While the direct gas-solid carbonation of natural minerals has not proven to be efficient, quite rapid conversions (60-80%) were obtained with calcium-containing Air Pollution Control (APC) residues at temperatures equal or above 350 °C and at a total pressure of 1 bar (Prigiobbe et al., 2009). The conversion calculations were based on the weight increase of the samples and on the maximum weight increase expected from the complete carbonation of the reacting phases. Among the various different waste materials (pulverized fuel ash, stainless steel slag, municipal solid waste incineration ash, and de-inking ash), the calcium oxide content of the waste material was found to be directly proportional to the degree of carbonation in the direct gas-solid carbonation[1] of these materials (Johnson, 2000). One exception was ground granulated blast furnace slag, which had the second highest CaO content, but resulted in the second lowest degree of carbonation. In addition, the direct gas-solid carbonation of municipal solid waste incineration (MSWI) bottom ash (Rendek et al., 2006) and fly ash (Li et al., 2007) has been studied with the purpose of combining the reduction of carbon dioxide emissions with the upgrading of the waste material. In both studies, carbonation was found to reduce the dangerous nature of the ash material (e.g., the leaching of heavy metals).

Stepwise gas-solid carbonation via $Mg(OH)_2$ has been proposed by Zevenhoven et al., (2006 and 2008). The research focuses on the use of a fluidized bed (FB) reactor for the carbonation of $Mg(OH)_2$ at up to 600 °C and 100 bar (allowing for super-critical conditions for CO_2) (Fagerlund et al., 2009). $Mg(OH)_2$ is produced by the solid-solid reaction of serpentine and ammonium sulphate at elevated temperatures (400-500 °C) to form magnesium sulphate (Equation 3), followed by the reaction of hydrated magnesium sulphate with a base (such as ammonium hydroxide) (Equation 4). The first tests with this method have been conducted and up to 63% conversion of $Mg(OH)_2$ produced from serpentinite has been reached (20 bar, 485 °C) (Fagerlund et al., 2010).

$$Mg_3Si_2O_5(OH)_4(s) + 3(NH_4)_2SO_4(s) \rightarrow 3MgSO_4(s) + 2SiO_2(s) + 5H_2O(l) + 6NH_3(g) \quad (3)$$

$$3MgSO_4(aq) + 6NH_4OH(aq) \rightarrow 3Mg(OH)_2(s) + 3(NH_4)_2SO_4(aq) \quad (4)$$

Probably the most widely studied mineral carbonation route is the *direct aqueous carbonation route*, which imitates and tries to enhance the slow natural carbonation of ultramafic rocks. In this process route, carbonic acid is used to extract metal cations from the mineral silicate. These cations then react with bicarbonate ions to form a solid carbonate. Carbonic acid is formed when carbon dioxide dissolves in water. For the magnesium silicate mineral olivine, these reactions are as follows: dissolution of carbon dioxide and formation of bicarbonate ion (Equation 5), extraction of Mg^{2+} cations (Equation 6), and formation of magnesium carbonate (Equation 7).

$$CO_2(g) + H_2O(l) \rightarrow H^+(aq) + HCO_3^-(aq) \quad (5)$$

$$Mg_2SiO_4(s) + 4H^+(aq) \rightarrow 2Mg^{2+}(aq) + H_4SiO_4(s) \text{ or } SiO_2(s) + 2H_2O(l) \quad (6)$$

$$Mg^{2+}(aq) + HCO_3(aq) \rightarrow MgCO_3(s) + H^+(aq) \quad (7)$$

A research group from the Albany Research Center (ARC) has investigated this route quite extensively (Gerdemann et al., 2004 and 2007; O'Connor et al., 2001, 2002, 2005a and 2005b). They found that with magnesium silicates the pH of the solution plays an important role and thus modified the solution chemistry from distilled water to a sodium

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[1] These experiments are here considered as "dry", because water to solid ratio seems to have been very low.

bicarbonate/sodium chloride solution (O'Connor et al., 2005b). In this new solution, the sodium bicarbonate slightly increased the alkalinity of the solution and acted as an effective CO_2 carrier, reducing the reaction time from 24 hours to 6 hours. The addition of the sodium chloride improved the extent of the carbonation reaction, although the reason for this was not clear. Calcium silicate (wollastonite) was found to be less affected by the solution chemistry. Serpentine carbonation was found to be improved significantly not only by heat treatment, but also by mechanical activation, while for olivine mechanical activation is the most suitable activation method that has been found (O'Connor et al., 2002). Optimized process conditions were presented for olivine (P_{CO2}=150 atm, T=185 °C, 0.64 M $NaHCO_3$ and 1 M NaCl), heat-treated serpentine (P_{CO2}=115 atm, T=155 °C, 0.64 M $NaHCO_3$ and 1 M NaCl) and wollastonite (P_{CO2}=40 atm, T=100 °C, distilled water) (O'Connor et al., 2005b). Of these three minerals, wollastonite was found to be the most reactive (Gerdemann et al., 2007). Additionally, Huijgen et al. (2006a) reported the 70% carbonation conversion of wollastonite in 15 minutes at 200 °C and a CO_2 pressure of 20 bar. Further, complete carbonation of synthesised larnite powders (calcium silicate) and larnite/silica aerogel composites was achieved in only 15 minutes of CO_2 flow at room temperature and atmospheric pressure using the aqueous route (Santos et al., 2009). It was concluded that the nanometric size of the active phase particles and the high specific surface area and porosity of the samples explain this rapid conversion. Nevertheless, under quite similar process conditions (155 °C, 158.6 bar of CO_2, 1 M NaCl and 0.64 M $NaHCO_3$) to those presented as optimal for olivine, the ultramafic rocks pyroxenite, hartzburgite, and dunite (containing minerals such as augite, diopside, lizardite, clinochrysotile, forsterite, olivine, and enstatite) showed very low carbonation conversion (Koukouzas et al., 2009).

Since the dissolution of silicate minerals such as serpentine and olivine is one of the main rate-limiting steps of aqueous carbonation, the enhancement of this step has been studied. Hänchen et al. (2006) found that the dissolution rate of olivine is approximately doubled at a low pH ($pH \leq 5$, at 120 °C) when a CO_2 atmosphere is used instead of nitrogen. Further, dissolved citrate, EDTA, and oxalate solutions were found to enhance the dissolution of antigorite serpentine under 20 bar of CO_2 at 120 °C; giving greater than 60% dissolution within 2 hours and near-complete dissolution within 10-20 hours (Krevor and Lackner, 2009).

Munz et al. (2009) studied the *stepwise aqueous carbonation of olivine*, where a H_2O-CO_2 solution was used to dissolve olivine at 130 °C, followed by the precipitation of magnesite in a separate reactor at 250 °C. The pressure was kept constant at 150 bar. The experimental results confirmed the dissolution of the olivine and the precipitation of magnesite, although detailed process parameters and conversions were not reported.

Several studies have been conducted in which the direct aqueous carbonation route is used for various different waste/by-product materials. Huijgen et al. (2005) found that within various process variables (particle size, temperature, P_{CO2}, stirring rate), particle size and reaction temperature were the most important ones for determining the carbonation rate of Linz Donawitz steel slag (i.e., basic oxygen furnace slag). The maximum carbonation conversion of Linz Donawitz steel slag (74%) was reached at a 19 bar CO_2 pressure and 100 °C within 30 minutes. The aqueous carbonation of Estonian oil shale ash has been studied quite extensively (Uibu et al., 2009; Uibu et al., 2010). Circulating fluidized bed combustion ash was found to be almost completely carbonated at atmospheric pressure and ambient temperature, while the inaccessibility of a portion of the free calcium as a result of the low porosity was assumed to be the reason for the less complete carbonation of the pulverized firing ash. The free calcium oxide content was found to be responsible for the largest part of the carbonation; however, other components were also discovered to take part in the binding of CO_2. The direct aqueous carbonation of alkaline paper mill waste converted all the $Ca(OH)_2$ of the starting material into calcite (Pérez-López et al., 2008).

Lackner et al. (1995) proposed *the use of acids or steam to extract the magnesium or calcium contents from the mineral prior to carbonation*. They focused on hydrochloric acid (HCl) because of its recoverability and inexpensiveness. When dissolved in HCl, magnesium silicate (here serpentine, as an example) forms magnesium chloride, water, and silica gel (Equation 8).

$$Mg_3Si_2O_5(OH)_4(s) + 6HCl(aq) \rightarrow 3MgCl_2(aq) + 2SiO_2(s) + 5H_2O(l) \qquad (8)$$

After the removal of the silica gel, either carbon dioxide could be introduced directly into the solution to produce magnesium carbonate or the solution could be used to produce hydroxides, followed by dry carbonation at high temperatures. In the latter case, the HCl is regenerated by boiling the water and excess acid from the solution, which is followed by decomposition of the solid magnesium chloride into magnesium hydroxide chloride (Mg(OH)Cl), HCl gas, and steam at 150 °C (Equation 9). The Mg(OH)Cl is then dissolved in water, forming solid magnesium hydroxide and a magnesium chloride solution (Equation 10). The solid magnesium hydroxide is carbonated at high temperatures (Equation 11) and the magnesium chloride is again cycled through the process.

$$MgCl_2 \cdot 6H_2O(s) \rightarrow Mg(OH)Cl(s) + HCl(g) + 5H_2O(g) \qquad (9)$$

$$2Mg(OH)Cl(s) \rightarrow Mg(OH)_2(s) + MgCl_2(aq) \qquad (10)$$

$$Mg(OH)_2(s) + CO_2(g) \rightarrow MgCO_3(s) + H_2O(g) \qquad (11)$$

Although the energy demand of the evaporation of the water has been considered too high, Lackner (2002) claimed that, since only low-grade heat is required, process integration could allow an energy penalty of less than 40% on a power plant using this sequestration method.

Wendt et al. (1998) suggested the *use of molten salt ($MgCl_2(H2O)_n$)* instead of HCl to reduce the overall water content of the HCl extraction process. The advantages of this were considered to be the natural acidity of the melt (making it possible to avoid the addition of HCl), lower water vapor pressures and the reduced water content of the system (reduced energy costs). However, it was concluded that heat pre-treatment of the rock was likely to be needed for extracting the magnesium content from the mineral, and the dilution of Mg(OH)Cl in water would be necessary for the formation of magnesium hydroxide and magnesium chloride. Direct carbonation in the melt was therefore thought of as an interesting alternative. For the time being, it seems that experiments with this route have not been made or at least they have not been reported in the published literature.

An experimental study of the use of HCl, as well as of another strong acid, nitric acid (HNO_3), for the extraction of magnesium from serpentinite (~83 wt-% serpentine, 14 wt-% magnetite) prior to the carbonation of the magnesium salt solution was carried out by Teir et al. (2007a and 2007b). In these experiments, serpentinite was dissolved in a 4 M solution of HNO_3 or HCl (Equation 12) at 70 °C, after which the excess solvent was evaporated, producing magnesium salt (Equation 13).

$$\begin{aligned} &Mg_3Si_2O_5(OH)_4(s) + 6(HNO_3/HCl)(aq) \\ &\quad \rightarrow 3Mg^{2+}(aq) + 6(NO_3^-/Cl^-)(aq) + 2SiO_2(s) + 5H_2O(l) \end{aligned} \tag{12}$$

$$\begin{aligned} &Mg^{2+}(aq) + 2(NO_3^-/Cl^-)(aq) + xH_2O(l) + y(HNO_3/HCl)(aq) \\ &\quad \rightarrow Mg((NO_3)_2/Cl_2)\cdot 6H_2O(s) + (x-6)H_2O(g) + y(HNO_3/HCl)(g) \end{aligned} \tag{13}$$

The precipitated salt was dissolved in water, which, in the case of the magnesium nitrate solution, resulted in the spontaneous precipitation of iron. From the magnesium chloride solution, most of the iron was precipitated with the help of the addition of NaOH. It was found that because of the acidity of the salt solution, the precipitation of carbonates required a pH increase by the addition of NaOH (Equation 14).

$$\begin{aligned} &5Mg((NO_3)_2/Cl_2)(aq) + 10NaOH(aq) + 4CO_2(g) \\ &\quad \rightarrow 10Na(NO_3/Cl)(aq) + Mg_5(OH)_2(CO_3)_4\cdot 4H_2O(s) \end{aligned} \tag{14}$$

In the optimal case, 0.9/1.1 g NaOH was used to produce one gram of precipitate containing 99/93 wt-% hydromagnesite ($Mg_5(OH)_2(CO_3)_4\bullet 4H_2O$) (in the experiment with HNO_3/HCl). The net conversion of serpentinite to hydromagnesite was 83% using HNO_3 and 70% using HCl (1 bar, 30 °C). While more than half of the acid was found to be easily recycled because of the evaporation, the consumption of the make-up chemicals (NaOH and HNO_3 or HCl) was calculated to be 2.4 t NaOH, as well as either 3.6 t HNO_3 or 2.1 t HCl per ton of CO_2 bound.

Serpentine has also been dissolved in sulphuric acid (H_2SO_4) and acetic acid (CH_3COOH) (Maroto-Valer et al., 2005). The solutions that were formed were found to contain large amounts of magnesium ions (the solution produced using H_2SO_4 contained more than the solution produced using CH_3COOH). However, although the solutions were neutralized with NaOH prior to carbonation at low temperature and pressure (20

°C, 36 atm with H_2SO_4 or 45 atm with CH_3COOH), the amounts of carbonate that were precipitated were found to be insignificant (<0.1% conversion).

The use of sulphuric acid for the production of a magnesium hydroxide ($Mg(OH)_2$) solution from serpentine for subsequent carbonation has also been investigated (Maroto-Valer et al., 2005). In this study, serpentine was dissolved in H_2SO_4 for 8 hours at 50 °C followed by filtration and the precipitation of $Mg(OH)_2$ with the help of NaOH. The $Mg(OH)_2$ precipitate (~ 35 wt-% MgO, 21 wt-% Na_2O) was dissolved in reverse osmosis water and carbonated at 20 °C and 45 atm for 3.5 hours. The calculated carbonation efficiency, which was based on the amount of magnesium in the precipitate, was 52.5%.

The so-called *pH swing process* was proposed by Park and Fan (2004 and 2005). In this process, a weak acid is used to dissolve magnesium from a magnesium-containing mineral with the aid of an internal grinding system (100-500-micron particle size, solution pH ~ 2, T~50-100°C, atmospheric pressure, <30 min). After the solid silica (SiO_2) is removed from the solution thus formed, the pH of the solution is slowly increased to precipitate iron oxide (pH ~ 8.4-8.8). Carbon dioxide at high pressure or flue gases containing carbon dioxide is introduced to the solution after the removal of the iron oxide. Finally, a pH suitable for the precipitation of carbonates is achieved by increasing the pH to ~ 9.5. Park and Fan (2004) reported the experiments, where 1.4 M ammonium bisulphate, as well as a mixture of 1 vol-% orthophosporic acid, 0.9 vol-% oxalic acid, and 0.1 vol-% EDTA solution, was used to dissolve serpentine (70 °C, 1 h) and NH_4OH was used to increase the pH. The carbonation product was relatively pure $MgCO_3{\cdot}3H_2O$. The overall carbonation conversion was 42% for 1.4 M ammonium bisulphate solvent and 65% for the solvent mixture.

The use of acetic acid to accelerate the carbonation of calcium silicates was proposed by Kakizawa et al. (2001). In the first step of this proposed process route, calcium silicate is dissolved in an acetic acid solution, generating a solution of calcium acetate and a solid residue of silicon oxide (Equation 15). To fix carbon dioxide as calcium carbonate, a carbon dioxide gas flow is introduced to the calcium acetate solution (Equation 16). This results in the precipitation of calcium carbonate and the regeneration of the acetic acid, which can then be recycled back to the first process step.

$$CaSiO_3(s) + 2CH_3COOH(aq) \rightarrow Ca^{2+}(aq) + 2CH_3COO^-(aq) + H_2O(l) + SiO_2(s) \quad (15)$$

$$Ca^{2+}(aq) + 2CH_3COO^-(aq) + H_2O(l) + CO_2(g) \rightarrow CaCO_3(s) + 2CH_3COOH(aq) \quad (16)$$

Acetic acid was considered to fulfill the extraction and carbonation requirements set for the acid: the acid has to be stronger than silicic acid, but weaker than carbonic acid. From the Gibbs free energy change calculations, it was found that both reactions ((Equation 15) and (Equation 16)) should process spontaneously at a CO_2 pressure of 1 bar and 25 °C. However, it was calculated that to obtain a higher $CaCO_3$ conversion (>40%), higher pressures were required. Kakizawa et al. reached about 48% calcium extraction from wollastonite in 250 minutes at 60 °C and at atmospheric pressure (22 wt-% acetic acid and 78 wt-% water). Using carbon dioxide pressures of 30 bar, a carbonation ratio of 20% was achieved in an hour at 60 °C. The determination of the amount of $CaCO_3$ formed was based on the weight increase of the filters used to filter the carbonated solution. The conversion ratio of $CaCO_3$ was found to be enhanced by the temperature and pressure increase, while the rate was found to suffer from the re-dissolution of $CaCO_3$ particles with increased reaction time.

Beard et al. (2004) suggested *the use of caustic alkali-metal hydroxide for the carbonation of metal silicates*. In this process route, caustic alkali-metal hydroxide is first reacted with metal silicate to produce the hydroxide of the metal. In the next process step, carbon dioxide is reacted with caustic alkali metal hydroxide to produce alkali metal carbonate. Finally, the hydroxide of the metal from step 1 is reacted with the alkali metal carbonate from step 2 to produce the carbonate of the metal originating from the metal silicate that was used. These reactions, for wollastonite, as a metal silicate, and NaOH, as an alkali-metal hydroxide, are as follows:

$$CaSiO_3(s) + NaOH(aq) \rightarrow NaCaSiO_3(OH)(s) \tag{17}$$

$$2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(aq) + H_2O(l) \tag{18}$$

$$\begin{aligned}&3NaCaSiO_3(OH)(s) + Na_2CO_3(aq) + H_2O(l)\\ &\qquad \rightarrow 4NaOH(aq) + CaCO_3(s) + NaCa_2Si_3O_8(OH)(s)\end{aligned} \tag{19}$$

The overall net reaction for wollastonite is therefore:

$$3CaSiO_3(s) + NaOH(aq) + CO_2(g) \rightarrow CaCO_3(s) + NaCa_2Si_3O_8(OH)(s) \tag{20}$$

The first reaction step was successfully tested with various calcium silicates (wollastonite, anorthite, labradorite, basalt, and fly ash), as well as with serpentine and olivine, using a sodium hydroxide solution (50 wt-%) (200 °C, total (fluid) pressure <15 atm, 72 h). The successful conversion of the reaction products of different calcium silicates from step one to carbonates was also demonstrated (200 °C, <15 atm, 72 h). $Mg(OH)_2$ (the reaction product of olivine and serpentine from step 1) did not produce $MgCO_3$ with $NaCO_3$ at 200 °C (<15 atm) as was expected, but it produced double carbonate eitelite ($Na_2Mg(CO_3)_2$) at pressures of 60-65 atm.

Yogo et al. (2005) suggested *the use of a weak-base strong-acid salt solution for the carbonation of calcium contents in industrial residues*. In the first step of this process route, calcium is extracted from the waste material by a weak-base strong-acid salt solution, such as NH_4Cl (Equation 21). Next, carbon dioxide reacts with the NH_4OH thus formed, producing $(NH_4)_2CO_3$ (Equation 22), which produces calcium carbonate by reacting with $CaCl_2$ from step 1 (Equation 23). The weak-base strong-acid salt used in the first process step is regenerated in step 3.

$$Ca_2SiO_4(s) + 2H_2O(l) + 4NH_4Cl(aq) \rightarrow SiO_2(s) + 2CaCl_2(aq) + 4NH_4OH(aq) \quad (21)$$

$$4NH_4OH(aq) + 2CO_2(g) \rightarrow 2(NH_4)_2CO_3(aq) + 2H_2O(l) \quad (22)$$

$$2(NH_4)_2CO_3(aq) + 2CaCl_2(aq) \rightarrow 2CaCO_3(s) + 4NH_4Cl(aq) \quad (23)$$

60% conversion of the calcium extraction reaction was reached with steel converter slag (44.5 wt-% CaO) as a source of calcium and an aqueous solution of ammonium chloride as the weak base-strong acid salt solution (Kodama et al., 2008). The extraction rate was found to increase with reduced particle size. The purity of the $CaCO_3$ that was generated was found to be 98% and the morphology of the particles appeared controllable. The energy consumption of the process was calculated to be 300 kWh/t CO_2. Both the power required for the grinding of the slag and the recovery and supply of NH_3, were found to be problematic.

A process in which *pressurized CO_2 is used to extract calcium from waste cement, followed by the precipitation of calcium carbonate at reduced pressure* has also been proposed (Iizuka et al., 2004). In this process route, waste cement is mixed with water, followed by the introduction of high-pressure carbon dioxide. As a result of the high solubility of $CaCO_3$ under high-pressure CO_2 conditions, calcium is extracted from the waste cement, but does not precipitate as calcium carbonate. After the residues are removed, the solution thus formed is left under low-pressure CO_2 conditions, resulting in the precipitation of $CaCO_3$. A higher waste cement-to-water ratio was found to increase the extraction rate but reduce the extraction ratio (Iizuka et al., 2004; Katsuyama et al., 2005). An increase in the CO_2 pressure and a decrease in the average size of the waste cement particles were found to increase the initial extraction rate. Approximately 50% calcium extraction was reached in seven minutes using a waste cement-to-water ratio of 0.29 wt-% at 3 MPa CO_2 pressure (50 °C) (Iizuka et al., 2004). The $CaCO_3$ precipitation rate was found to be only slightly dependent on the stirring rate. However, the rate was found to be increased by increased temperature and reduced by increased pressure (Katsuyama et al., 2005). The calcium carbonate content of the produced precipitates was about 98% (Katsuyama et al., 2005).

2.1.4 Comparison of different mineral carbonation methods

Different mineral carbonation methods, together with their main advantages and disadvantages, are collected in Table 1. Direct gas-solid carbonation does not seem to be an effective carbonation method for natural magnesium silicates. This is unfortunate, since this method could possibly produce high-temperature heat simultaneously with carbonation. However, it might be suitable for certain waste materials, which could also benefit from its possible capability to reduce the dangerous nature of the materials. Stepwise gas-solid carbonation via $Mg(OH)_2$ seems interesting as it should be suitable for natural magnesium silicates and produce high-temperature heat and it might not consume significant amounts of chemicals. So far, however, the heat requirement for

$Mg(OH)_2$ production is significantly higher than what is generated during the carbonation (Zevenhoven et al., 2010).

The simplicity of the direct aqueous carbonation route, as well as the quite promising results reached with this route, indicates that this route is still worth exploring. Even so, as long as the raw material is carbonated in one step, the end product is unlikely to be pure carbonate. In addition, it seems that certain process conditions are suitable only for certain raw materials, something which seems to be common to many of the proposed mineral carbonation process routes, i.e., there might be a need to find a specific process route or at least the process conditions for each raw material type.

Indirect mineral carbonation methods aimed at natural magnesium silicates and based on acids as solvents seem to extract the reactive element efficiently from the silicate. On the other hand, they suffer from unfavorable carbonation conditions, since the precipitation of carbonates is not favored under acidic conditions. The addition of a base neutralizes the acidity, but makes the recycling and re-use of the chemicals impossible or very expensive. The process route based on the use of caustic alkali-metal hydroxide also suffers from the chemical consumption. Previous literature indicates that acetic acid-based calcium silicate carbonation could have potential as the solution formed from the acetic acid and calcium silicate should be alkaline.

Both process routes, i.e., one using a weak-base strong-acid salt solution and the other using pressure change, seem to be able to produce pure calcium carbonate from certain industrial waste materials efficiently. The recovery of the evaporated NH_3 might, however, hinder the economically viable use of the former process route. The latter process route is not reported to consume any chemicals, but it needs pure carbon dioxide, which means that expensive CO_2 capture methods are required. This problem is also present with the direct process routes that require high pressures. Overall, many mineral carbonation methods have been proposed and studied, and few of them seem promising, while none is yet above the others.

Table 1. Main advantages and disadvantages of different mineral carbonation methods.

Method	Route	Materials tested	Advantages	Disadvantages
Direct	Gas-solid	Serpentine, APC residues, MSWI ash…	Upgrading of the waste material	Slow with natural minerals
	Aqueous	Serpentine, olivine, wollastonite, steel slag, Estonian oil shale ash…	Quite simple process, promising results	End product probably not pure carbonate, High pressure-based routes require pure CO_2
Indirect	Stepwise gas-solid carbonation via $Mg(OH)_2$	Serpentinite	High-temperature heat produced during carbonation, promising results	Heat requirement of $Mg(OH)_2$ production
	Acid as solvent	Serpentinite, serpentine, wollastonite	Reactive element extracted efficiently, pure end product	Carbonation step requires addition of base, although acetic acid route has potential for calcium silicates
	Molten salt	-		Experiments not reported in published literature
	Caustic alkali-metal hydroxide	Serpentine, olivine, wollastonite…		Consumes chemicals
	Weak-base strong-acid salt	Steel slag	Promising results, pure end product	Evaporation of NH_3?
	Pressure change	Waste cement	Promising results, pure end product	Requires pure CO_2

2.2 Steelmaking slags

Steelmaking slags are generated in the steel manufacturing process. Steel manufacturing is one of the biggest industries in the world, producing more than one billion tonnes of steel annually (International Iron and Steel Institute, 2007). Most of the steel is produced either via the integrated process route (Figure 2) or via the electric arc furnace route. In the integrated process route steel is manufactured from iron ore, while in the electric arc furnace route recycled steel is used as the raw material for steel.

Steelmaking slags can be divided into two main types, blast furnace slag and steel slag. In a blast furnace, iron ore is reduced into molten iron using coke as the primary reducing agent (NSA, 2009a). Lime, in the form of flux stone (limestone or dolomite), is charged into the furnace, forming blast furnace slag as it reacts, for example, with the silicates and impurities of the iron ore. Molten iron and blast furnace slag are tapped from the bottom of the furnace. Since slag is lighter than molten iron, it is quite easily separated.

Steel is produced from iron, scrap, and lime, either in a basic oxygen furnace or in an electric arc furnace (NSA, 2009b). In the former, oxygen is blown into the furnace to burn off the carbon from the molten iron, thus producing low-carbon steel. In the electric arc furnace, electricity is used to melt scrap metal into steel. In both cases, steel slag is generated simultaneously with the steel as the lime reacts with the impurities. These slags are generally named after the process they are generated by. Besides basic oxygen furnace slag (also called steel converter slag) and electric arc furnace slag, desulphurization slag and ladle slag can also be generated during steel manufacturing. Desulphurization slag is formed in the integrated process route, when sulphur is removed from the iron by using lime. Ladle slag is formed when oxygen is removed with aluminum in the ladle furnace before the steel is cast into slabs.

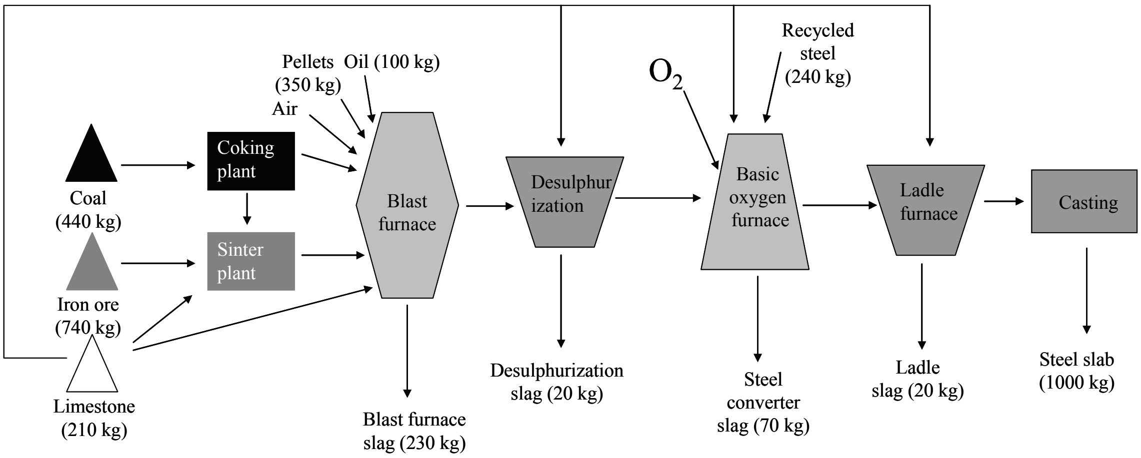

Figure 2. Simplified schematic diagram of the integrated steel manufacturing process (rough values of some of the raw material and by-product streams are presented in parentheses).

Slags are removed from the processes in their molten phase and then cooled down before crushing and screening. While the chemical properties of the slags are dependent on the compositions of the raw materials and the process step they are generated in, their physical characteristics vary depending on the slag processing (i.e., the cooling method used, crushing, and screening). Steel slags are typically cooled by air cooling i.e., poured into a pit and allowed to cool down in air. Cooling is sometimes enhanced by spraying water onto the slag. Blast furnace slag can also be cooled down by a granulation method, in which it is rapidly cooled down by using large quantities of water, forming glass-like particles. After cooling, slags are processed to remove all free metallics, after which the grain size of the slag is generally less than 10 cm (The European Slag Association, 2006). Depending on the needs of the customer, slags can be ground to a selected grain size.

Blast furnace slag contains mainly calcium, aluminum, and magnesium in the form of silicates, while the principal constituents of steel slags are calcium silicates, calcium aluminoferrites, and fused oxides of calcium, iron, magnesium, and manganese (Lewis, 1982). Steel slags usually also include free calcium oxide. Additionally, the structure of granulated blast furnace slag is typically non-crystalline.

Both blast furnace slag and steel slag can be used to replace aggregates in various kinds of construction applications (NSA, 2009a and 2009b). Steel slags are also suitable as a source of iron and flux materials in blast furnaces (Lewis, 1982) and for improving soil quality in agriculture (NSA, 2009b), while granulated blast furnace slag can even be used as a partial replacement for, or additive to, Portland cement (Rao, 2006). Free oxide phases in steel slag can cause expansion, restricting their use in construction applications requiring very stable conditions. The possible leaching of heavy metals can also restrict the utilization of steelmaking slags.

Finland has a relatively large steel industry sector, with four steelmaking plants in operation. Those plants produced a total of about 4.8 Mt of steel in 2004 (Teir, 2008). Most of the steel manufactured in Finland, produced at the Ruukki mill in Raahe and the Ovako Steel mill in Koverhar, is manufactured from iron ore and recycled metal via the integrated process route. The Ovako Steel mill at Imatra manufactures steel from scrap metal with an electric arc furnace process. In addition, the Outokumpu mill, situated in Tornio, uses recycled metal and ferrochrome to manufacture stainless steel. Together these mills produce approximately 1.6 Mt of steelmaking slags per year (Rinne, 2008). If all these slags could be used to manufacture PCC, ideally about 1.1 Mt of calcium carbonate would be produced and 0.5 Mt of CO_2 could be fixed annually.

2.3 Precipitated calcium carbonate

2.3.1 Properties

As a paper filler and coating pigment, PCC is used to improve the quality of paper (Roskill, 2008). Fillers are needed, for example, to improve the whiteness, opacity, brightness, and color of the paper, as well as for replacing some of the cellulose, which is typically more expensive. Coating is needed to provide a smooth and ink-receptive surface for the paper. While the demand for coating-grade PCC is increasing, PCC is currently mostly used as a filler.

The clear advantage of PCC over other fillers and coating pigments is its versatility. While other pigments are prepared by physical methods such as grinding, PCC is synthesized, and thus its properties can be more easily controlled. The main properties of the PCC that can be altered to meet performance criteria are particle size, particle shape, surface area, surface chemistry, and particle size distribution.

There are three different polymorphs of calcium carbonate: calcite, aragonite, and vaterite (Casey, 1983; Imppola, 2000). Commercial precipitated calcite typically has a rhombohedral, prismatic, or scalenohedral crystal type, while aragonite is typically in needle-like particle form, with a high aspect ratio (length-to-width ratio) (Figure 3). Vaterite is not used commercially. The benefits of aragonitic PCCs include good fiber coverage and loose coating layer packing (Imppola, 2000). The former improves the surface smoothness of the paper and thus forms a high gloss, while the latter gives high light scattering (~high opacity) and an ink-setting rate that is different from that of the other pigments. Scalenohedral calcite is used to adjust the brightness, opacity, bulk, and sizing of the paper (Roskill, 2008). The prismatic crystal type allows an increase in productivity and improves the dry strength of the paper. The rhombohedral particle shape increases the brightness, strength, and filler loading of the paper, and improves runnability and sizing. The different advantages of these morphologies can be combined by mixing them.

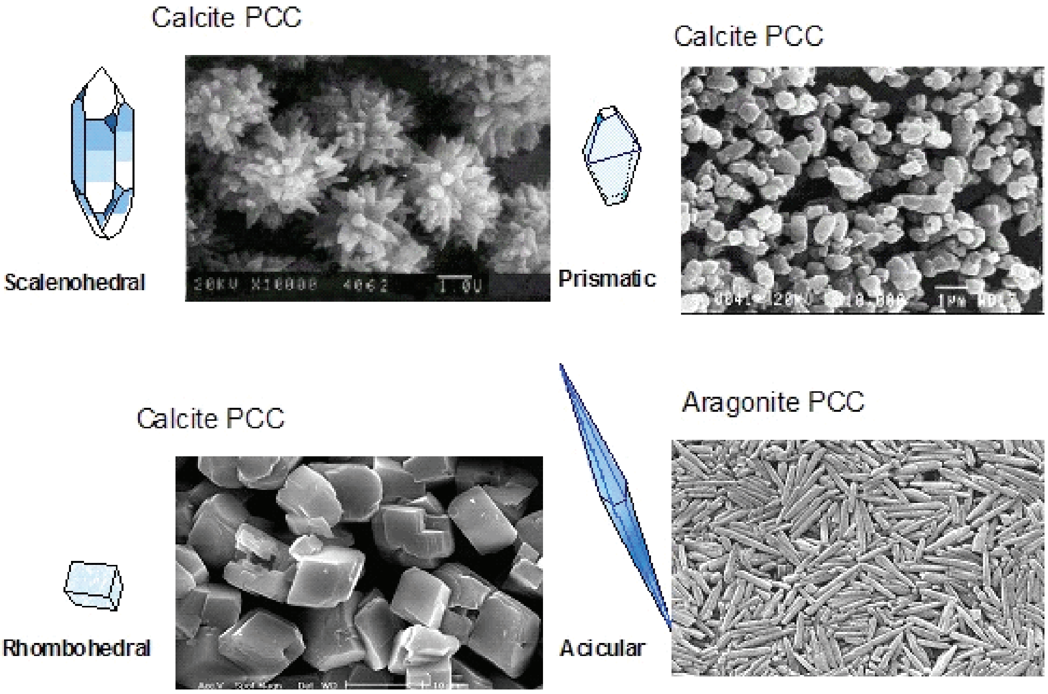

Figure 3. Four different crystal shapes of precipitated calcium carbonate (Specialty Minerals, 2008).

2.3.2 Production processes

There are basically three different methods of PCC production (Figure 4): the carbonation process, the lime-soda process, and the calcium chloride-sodium carbonate double salt decomposition process (Casey, 1983). All of these methods use milk of lime ($Ca(OH)_2$) to produce PCC. Milk of lime is produced from limestone by calcination and slaking. The limestone is selected on the basis of its chemical purity, color, and the size required for a given lime kiln. In the calcination step, limestone is decomposed into lime (CaO) and carbon dioxide gas in the kiln at high temperature (Equation 24). After calcination, the lime is screened to remove impurities originating from the limestone. Milk of lime is finally produced by slaking the lime in water (Equation 25). The purity, activity, particle size, concentration, and temperature of the milk of lime all affect the physical properties of the end product PCC, giving great importance to the control of these parameters in its manufacture.

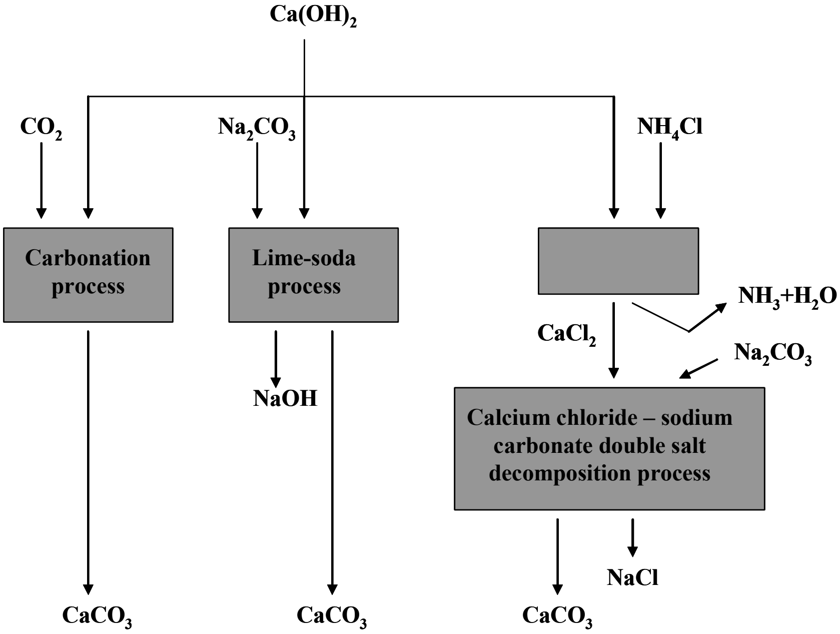

Figure 4. Basics of the three different methods of PCC production (Eloneva, 2008).

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \tag{24}$$

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) \tag{25}$$

In the carbonation process, carbon dioxide is bubbled through the calcium hydroxide slurry, producing a calcium carbonate precipitate (Equation 26). Flue gases from the power plant, lime kiln, or recovery kiln are typically used as a source of carbon dioxide (Imppola, 2000). The CO_2 content of the flue gases should be above 10% and they should not contain sulphur (Roskill, 2008). So-called satellite plants, where PCC is manufactured near the paper mill from transported lime, are of increasing interest (Imppola, 2000). This is a consequence of the reduced costs of shipping. The carbonation method is the most widely used, because it uses the most readily available and cheapest raw materials (Casey, 1983). However, the process is actually quite complex, since the physical properties of the PCC are controlled by the initial solution temperature, temperature profile, concentration of reactants, pH, agitation method, gas introduction speed, time, and the addition of auxiliary materials (Casey, 1983; Roskill, 2008).

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l) \tag{26}$$

The lime-soda process has been used by commercial alkali manufacturers to produce caustic soda as an alternative to the chlor-alkali process. In this process, milk of lime is reacted with sodium carbonate to produce sodium hydroxide (NaOH) and calcium carbonate (Equation 27). While it is possible to produce the desired particle size of PCC by this method, it is partly done at the expense of the recovery of sodium hydroxide. The process step of the kraft recovery cycle, where green liquor is converted into white liquor (recausticization), follows the same reaction as the lime-soda process (Equation 27); some paper mills use this calcium carbonate for paper coating. In practice, this PCC is not readily suitable to be used for this purpose. Its alkali content has to be neutralized and grit removed by classification.

$$Ca(OH)_2(aq) + Na_2CO_3(aq) \rightarrow 2NaOH(aq) + CaCO_3(s) \tag{27}$$

The simplest PCC production method is the calcium chloride-sodium carbonate double salt decomposition process, in which calcium chloride solution is reacted with a soda ash solution to produce a calcium carbonate precipitate and sodium chloride (Equation 28). The calcium chloride needed in the process is produced by reacting milk of lime with ammonium chloride (Equation 29). Commercial plants are dependent on a low-cost source of calcium chloride, and are therefore located close to Solvay process plants, which produce calcium chloride as a by-product of soda ash manufacture. The quality of the produced calcium carbonate can be controlled by addition times, the agitation method, pH, concentrations, and reaction temperatures.

$$CaCl_2(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + CaCO_3(s) \tag{28}$$

$$Ca(OH)_2(aq) + 2NH_4Cl(aq) \rightarrow CaCl_2(aq) + 2NH_3(g) + 2H_2O(l) \tag{29}$$

All three of these PCC production methods require careful control in order to attain a product suitable for paper applications.

Besides the three main PCC production methods, there are a couple of alternative methods on trial based on different waste streams. In the CalciTech process carbide lime waste (i.e., impure $Ca(OH)_2$) from the production of acetylene gas from calcium carbide is purified by either heat-treating the dry powder waste or by processing the wet slurry chemically (Roskill, 2008). The purified product is suitable for PCC manufacturing. Envirofil® PCC is manufactured from incinerator mineral ash residue from the incineration of de-inking residue. In the European Union's SERECARB research project the objective is to develop a new process for PCC production based on the recovery of calcium carbonate from paper mill effluents and sludge.

Gao et al. (2007) proposed the utilization of the distiller waste and residual mother liquor from the soda ash industry for the production of PCC and for the reduction of environmentally dangerous wastes (Equation 30). It was concluded that the use of a surfactant was necessary for the production of spherical ultrafine calcium carbonate precipitate from the distiller waste and residual mother liquor. Lower temperatures were found to produce smaller particles. Reaction time and mixing processes were also considered to have an effect on the average size of the particles.

$$\left(NH_4\right)_2CO_3(aq) + CaCl_2(aq) \rightarrow 2NH_4Cl(aq) + CaCO_3(s) \qquad (30)$$

The production of PCC from alkaline ash transportation waters of Estonian power production has been proposed and studied by Uibu et al. (2009 and 2010) as a means to enhance the neutralization of these waters. The reactor type was found to affect the particle size (using a barboter-type reactor resulted in slightly larger particles than when a dispergator-type reactor was used) and shape (the presence of SO_2 in flue gases caused agglomeration in a dispergator-type reactor). The $CaCO_3$ content of the precipitates was 86-94%.

3 Focus of the present thesis

While the carbon dioxide emissions from steel manufacturing are large, significant reductions could be achieved by using steelmaking slags for carbon dioxide mineralization. If calcium could be extracted from the slags prior to carbonation, a pure, and thus also marketable, calcium carbonate might be produced. This could possibly replace some of the natural and synthetic $CaCO_3$ used in industry, combining savings in natural resources with a reduction of CO_2 emissions.

The objective of the research reported in this thesis was to investigate the possibility of reducing CO_2 emissions by utilizing steelmaking slags as raw material for CO_2 mineralization. The target was that the end product of the CO_2 mineralization would be a pure calcium carbonate suitable for utilization.

When the research reported in this thesis started, the acetic acid process route, proposed by Kakizawa et al. (2001), seemed to be the most promising calcium silicate-based carbonation route (Teir et al., 2005). However, the quality and purity of the produced precipitate was not reported by Kakizawa et al. and suitability of the route for steelmaking slags had not been tested. Therefore, the first goal was to find out whether the acetic acid process route would be a suitable method for producing pure calcium carbonate from steelmaking slags and reducing CO_2 emissions.

The research tasks for achieving this were:

- to study the ability of acetic acid to dissolve calcium from steelmaking slags. The steelmaking slags in focus were the two major slag types from the integrated steel manufacturing process route, i.e., blast furnace slag (Paper I) and steel converter slag (Paper III);

- to study the precipitation of calcium carbonate (i.e., the sequestration of CO_2 as $CaCO_3$) from a solution produced by using steelmaking slag and acetic acid (Papers II and III);

- to study the feasibility of the acetic acid-based steelmaking slag carbonation (Papers II and III).

On the basis of the findings of the acetic acid process route research, the key issue for developing a feasible process for producing pure calcium carbonate from steelmaking slags with negative CO_2 emissions seemed to be finding an effective calcium-selective solvent that can be fully recovered and reused. Consequently, the second goal was to find a solvent that dissolves calcium selectively from the slag and allows $CaCO_3$ to precipitate from the solution thus formed without any need for additives that prevent the efficient recycling and re-use of the solvent (Paper IV). Once the promising solvents had been found, the feasibility of the method based on these solvents was investigated

(Paper V). The utilization of steelmaking slags as the raw material for carbon dioxide mineralization will change the quality of the slags. It is desired to produce a slag residue that is not environmentally harmful. Thus special attention was paid to the quality of the slag residue in the method that was investigated (Paper VI).

4 Acetic acid process route

The possibility of using the acetic acid process route for fixing CO_2 as pure calcium carbonate with steelmaking slags as a raw material is studied in this chapter. The ability of acetic acid to dissolve calcium from the two major slag types from the integrated steel manufacturing process route, i.e., blast furnace slag and steel converter slag, is experimentally investigated. Besides this, the precipitation of $CaCO_3$ from a solution produced by using steelmaking slag and acetic acid, i.e., the sequestration of CO_2 as $CaCO_3$, is studied experimentally and by thermodynamic equilibrium calculations. Finally, the feasibility of the acetic acid-based steelmaking slag carbonation is assessed.

4.1 Ability of acetic acid to dissolve calcium from blast furnace slag and steel converter slag

4.1.1 Description of the experiments

The ability of acetic acid to dissolve calcium from steelmaking slags was investigated by dissolving blast furnace slag or steel converter slag in various concentrations of an aqueous solution of acetic acid (Figure 5). The slag, ground to a specific grain size, was added to a glass reactor containing a particular concentration of acetic acid at the desired temperature. The glass reactor was surrounded by an open water bath, which was heated using a separate temperature-controlled water bath (Figure 6). To avoid evaporation losses, the reactor was equipped with a condenser cooled with tap water. A magnetic stirrer was used for stirring the solution. The pH and temperature of the solution were measured using electrodes, allowing the real-time monitoring and logging of data. A nitrogen gas bottle was connected through a flow rate controller, allowing nitrogen to be bubbled through the solution.

The steelmaking slags used in the experiments were blast furnace slag and steel converter slag provided by the Raahe Works (Figure 7). The compositions of the slags were analyzed using X-ray diffraction (XRD) and X-ray fluorescence spectroscopy (XRF). The slag samples were digested and the calcium (Ca), iron (Fe), silicon (Si), magnesium (Mg), manganese (Mn), aluminum (Al), and vanadium (V) contents were analyzed using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The steel converter slag was also analyzed by means of a Scanning Electron Microscope (SEM).

Various samples of the solution were taken during the course of the experiments to observe the progression of the dissolution. The solution samples were filtered and analyzed for Ca, Fe, Si, Mg, Mn, Al, and V by using ICP-AES. Two hours after the slag had been added, the experiment was stopped. The parameters of the dissolution experiments are shown in Table 2, while more detailed descriptions of the experiments are presented in Papers I and III for blast furnace slag and steel converter slag, respectively.

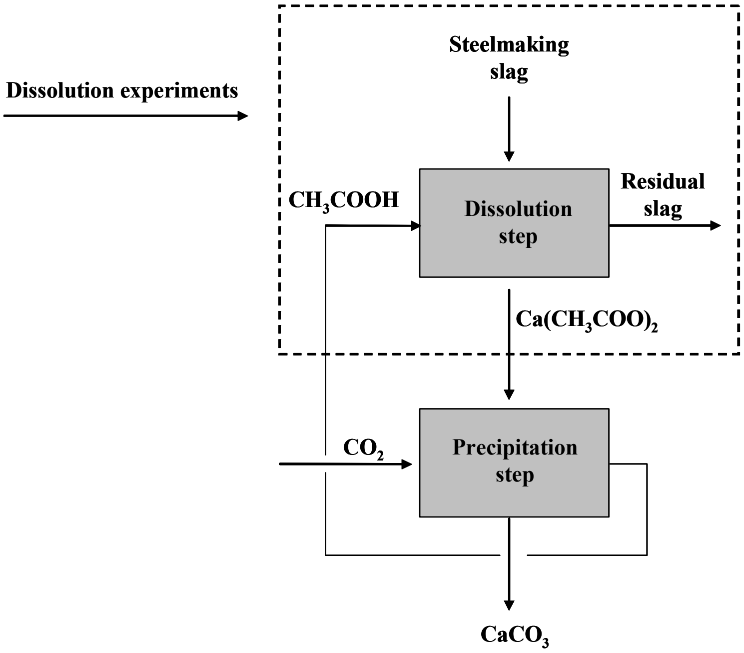

Figure 5. Process step in the acetic acid process route studied in the dissolution experiments (marked with dashed line) (Eloneva, 2008).

Figure 6. Photo of the test facility used for experiments performed under atmospheric pressure conditions (Eloneva, 2008).

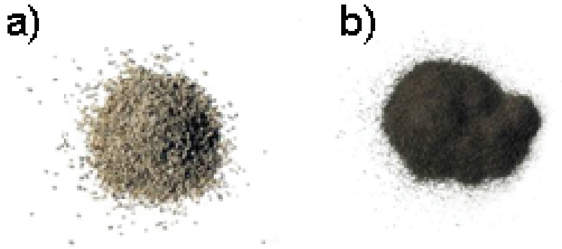

Figure 7. Photos of a) ground blast furnace slag and b) ground steel converter slag provided by the Raahe Works.

To analyze the composition of the residual (i.e., undissolved) slag, a large batch of steel converter slag (300 g, grain size <1 mm) was dissolved in acetic acid solution (1 M, 1.5 l) at 30 °C. A mechanical stirrer was used to ensure proper mixing. After two hours, the stirrer was turned off and the residual slag was removed from the solution by sedimentation and filtration. A sample of the residual slag was dried in an oven at ~120 °C and sent for both XRD and SEM analysis.

Table 2. Parameters of dissolution experiments (Eloneva, 2008).

Steelmaking slag (type)	Mass of the steelmaking slag (g)	Grain size (µm)	Solution (l)	Acetic acid (mol/l)	Solution temperature (°C)
Blast furnace slag	4.2	350-500	0.25	0, 0.0070, 0.70, 1.7, 5.8	50
Blast furnace slag	4.2	350-500	0.25	0.70	30, 70
Steel converter slag	10	125-250	0.5	0, 0.1, 0.5, 2, 4, 6, 8	30
Steel converter slag	10	125-250	0.5	0.1	50, 70

4.1.2 Characterization of the slags

The XRD and XRF analyses of the blast furnace slag showed that it consisted mostly of Ca, Si, Mg, and Al in amorphous phases (Table 3). XRD analysis of the steel converter slag showed that it consisted of lime (CaO), calcium hydroxide ($Ca(OH)_2$), quartz (SiO_2), wuestite (FeO), calcium iron oxide ($Ca_2Fe_2O_5$), and larnite (Ca_2SiO_4). According to XRF (Table 3) and ICP-AES (Table 4) analyses, the iron content of the steel converter slag was high, while the contents of manganese, silica, and aluminum were more moderate when compared to their contents in the blast furnace slags. The calcium content was high in both slag types.

Table 3. Composition (wt-%) of the blast furnace slag and steel converter slag expressed partly in terms of oxides as determined by XRF analysis* (Eloneva, 2008).

Element	Blast furnace slag	Steel converter slag
CaO	40.6 (±0.7)	45.9 (±0.7)
SiO_2	34.1 (±0.8)	13.9 (±0.3)
MgO	10.7 (±0.4)	3.7 (±0.1)
Al_2O_3	9.4 (±0.3)	2.0 (±0.1)
S	1.7 (±0.1)	
TiO_2	1.7 (±0.1)	
Fe	0.63 (±0.03)	16.6 (±0.2)
K_2O	0.6 (±0.1)	
F		6.1 (±0.5)
Mn	0.4 (±0.05)	2.3 (±0.1)
V		0.98 (±0.06)

*Only elements present at >0.1 wt-% are shown.

Table 4. Contents of selected elements in blast furnace slag and steel converter slag according to ICP-AES analysis (Eloneva, 2008).

Element	Blast furnace slag wt- % (±0.1)	Steel converter slag wt- % (±0.1)
Ca	27.9	30.1
Fe	0.1	14.4
Si	12.0	5.0
Mg	7.2	2.8
Mn		2.2
Al	2.3	1.2

4.1.3 Experiments with the blast furnace slag

Immediately after the blast furnace slag was added to the acetic acid solution, the pH of the solution rose (1-3 pH units) (Figure 8) (Paper I). The solution temperature of most of the acetic acid solutions also rose (1-2 °C), indicating the occurrence of an exothermic reaction. The final pH value of the weakest acetic acid solution was significantly higher (~ 6-8 pH units) than that of the other acetic acid solutions (pH 2-4).

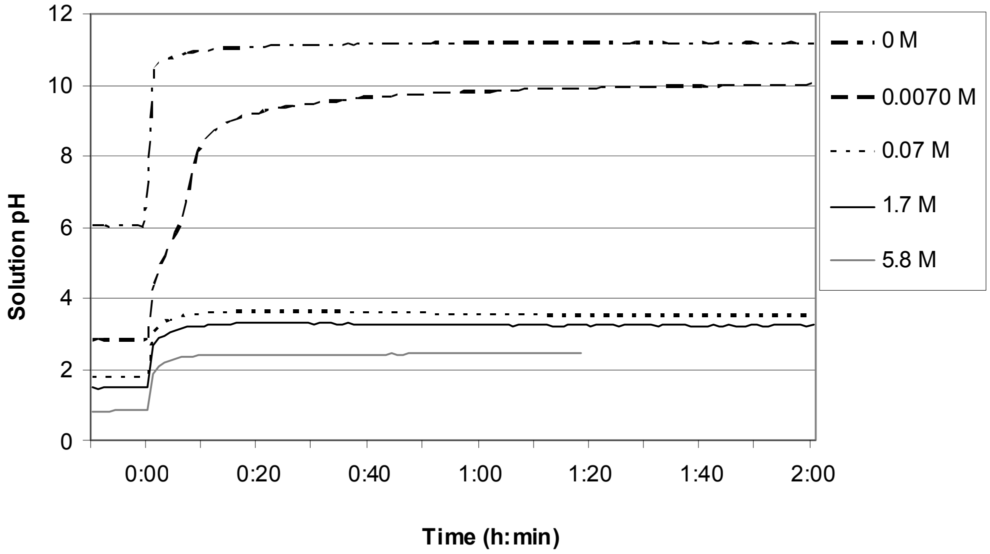

Figure 8. pH recordings of dissolution experiments at 50 °C in various concentrations of acetic acid (250 ml) (4.2 g blast furnace slag added at 0:00). (Experiment with 5.8 M solution lasted for two hours, but the data of the pH recordings were accidentally deleted after about one hour.)

The results from the ICP-AES analyses show that the strength of the acetic acid solution has a significant effect on the extraction of the calcium (Figure 9). Distilled water and the weakest acetic acid solution dissolved only a small proportion (1 and 2%, respectively) of the calcium in the slag during the total of two hours that the experiment lasted, while the 0.70 M acetic acid solution dissolved about 55% and the strongest acetic acid solutions dissolved most of the calcium within five minutes of the slag being added into the solution. The calcium extraction efficiency of over 100% reached with the two strongest solutions can be explained by the heterogeneity of the blast furnace slag that was used. Approximately 15 mol CH_3COOH per mol of calcium, i.e., ~10 g slag/mol CH_3COOH, seems to be enough for the complete dissolution of the calcium in blast furnace slag.

The solution temperature also had a significant effect on the dissolution of the calcium (Figure 10). At 30 °C, dissolution was slower than at 50 °C, but the final calcium extraction efficiency was higher (~ 9 %-units). At 70 °C, most of the dissolved calcium had dissolved within five minutes of the addition of the blast furnace slag, but the extraction efficiency was clearly less than at 50 °C or at 30 °C. On the basis of these results, it can be seen that the higher the temperature, the higher the rate of dissolution, and the higher the temperature, the lower the solubility of the calcium.

Those acetic acid solutions that were able to dissolve calcium efficiently dissolved some part of the other measured elements as well (Figure 11). Significant amounts of aluminum and magnesium were dissolved from the blast furnace slag in all these acetic acid solutions, and the strongest solution also dissolved significant amounts of the silica. While the amount of iron dissolved was small, it was a clear proportion of the iron in the slag and was enough to color the solution.

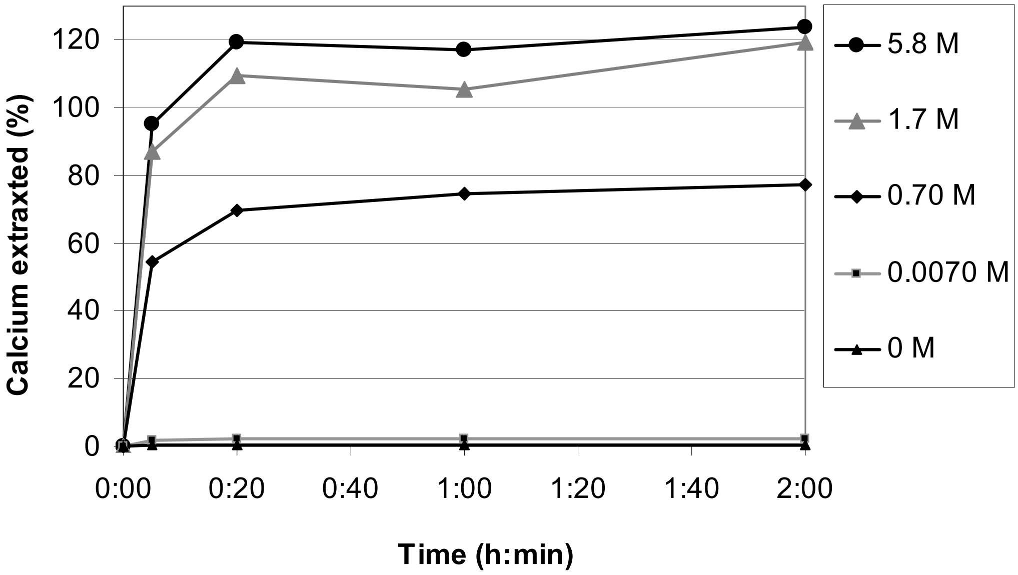

Figure 9. Dissolution of the calcium from the blast furnace slag (4.2 g) in acetic acid solution (250 ml) of various concentrations at 50 °C (Eloneva, 2008).

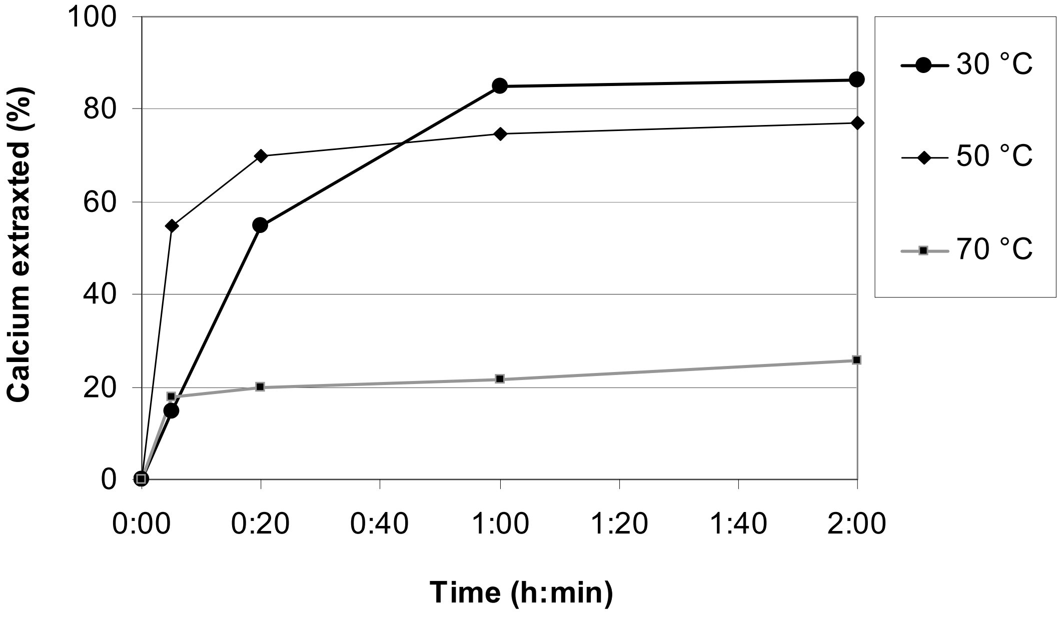

Figure 10. Effect of solution temperature on dissolution of calcium from blast furnace slag (4.2 g) in 250 ml of 0.70 M solution of acetic acid (Eloneva, 2008).

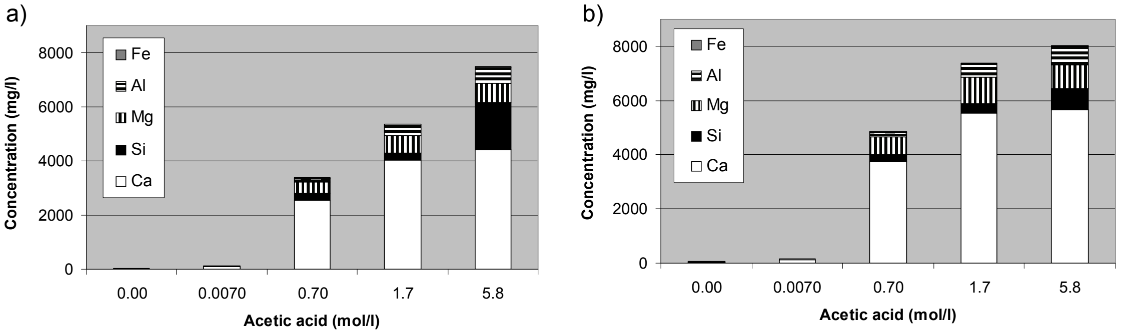

Figure 11. Dissolution of the selected elements from blast furnace slag (4.2 g) in various concentrations of acetic acid (250 ml) at 50 °C a) five minutes and b) two hours after the slag was added (Eloneva, 2008).

Silica was the only measured element, the concentration of which decreased with time (in the strongest acetic acid solution). This, coupled with observations of the formation of a gel phase, indicates that longer leaching times promote the formation of silica gel. The silica concentration also decreased during the experiment with 0.70 M acetic acid solution at 30 °C. While the temperature of the solution did not seem to have any significant effect on the dissolution of the aluminum, the dissolution of the magnesium was clearly temperature-dependent, the dissolution being the greatest at the lowest solution temperature.

4.1.4 Experiments with the steel converter slag

Similarly to the experiments with the blast furnace slag, the temperature of the solution and pH rose (1-3 °C and 1-2 pH units, respectively) immediately after the steel converter slag was added to the acetic acid solution (Figure 12) (Paper III). The pH of the 0.1 M acetic acid solutions continued to increase after the initial increase. The pH increase was faster at 50 °C and at 70 °C than at 30 °C. The final pH values of the 0.1 M solutions were also significantly higher (from two to four times) than those of the other acetic acid solutions. While the solution temperature of the distilled water did not rise after the addition of the slag, the pH increase was significant (~7 pH units).

According to the results from the ICP-AES, calcium leached rapidly (within two to ten minutes) from the steel converter slag in every solution that was tested (Figure 13). Similarly to the experiments with the blast furnace slag, the strongest acetic acid solutions (2-8 M) dissolved calcium efficiently (86-90%), although, unlike with the blast furnace slag, 100% calcium extraction was not reached. Distilled water and weaker acetic acid solutions (0.1 M and 0.5 M) were also able to dissolve some calcium, from 9 to 52%, from the steel converter slag.

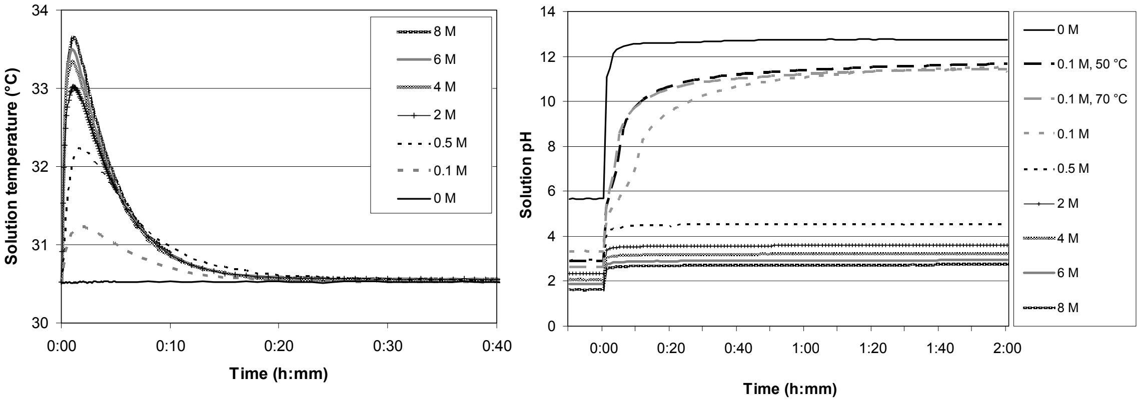

Figure 12. Temperature recordings of dissolution experiments at 30 °C and pH recordings of dissolution experiments at 30 °C, 50 °C, and 70 °C in various concentrations of acetic acid (500 ml) (10 g steel converter slag added at 0:00).

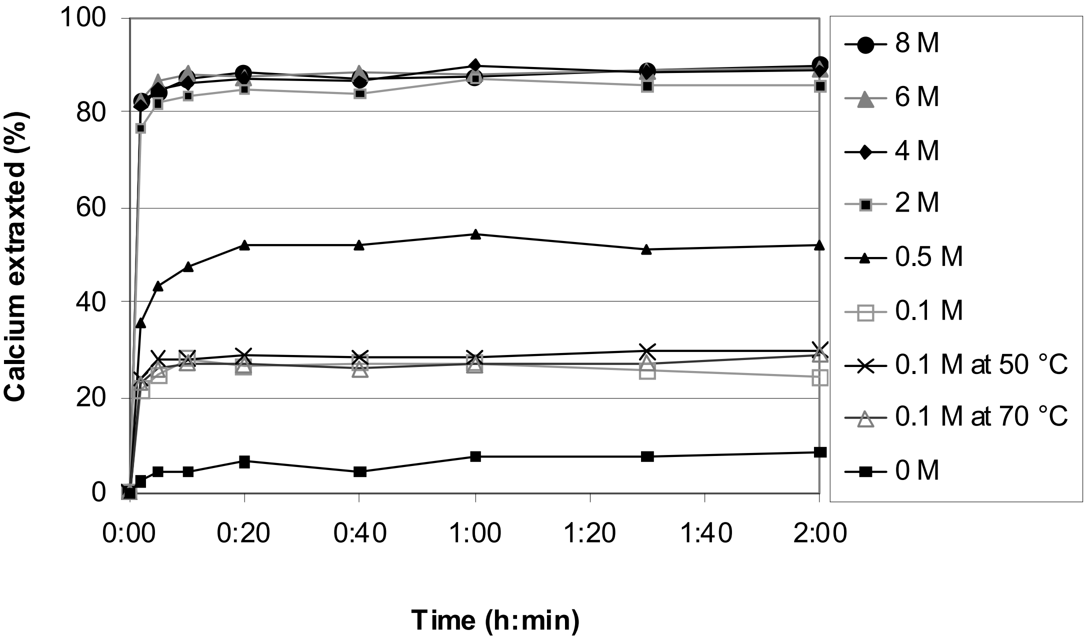

Figure 13. Dissolution of the calcium from the steel converter slag (10 g) in acetic acid solution (500 ml) of various concentrations at 30 °C (dissolution in 0.1 M solutions also at 50 °C and 70 °C) (Paper III).

The strength of the acetic acid solution had a clear effect on the dissolution of the measured elements. The weakest acetic acid solution and distilled water dissolved calcium quite selectively from the slag, while stronger solutions dissolved all the other measured elements as well (Figure 14). Although the concentrations of the Mn, Mg, V, and Al were also small when stronger acetic acid solutions were used (2-8 M), considerable amounts of Fe and Si were dissolved. All the measured elements dissolved in a similar manner from the steel converter slag in the weakest acetic acid solution at all solution temperatures, although, at 50 °C, the calcium concentration was slightly higher than at 30 or 70 °C. The dissolution behavior of Si confirmed the results achieved with the blast furnace slag, which indicated that a longer leaching time promotes silica gel formation, although, unlike with blast furnace slag, this behavior was observed in the weakest acetic acid solution.

XRD analysis of the residual slag showed that it contained quartz, wuestite, calcium iron oxide, larnite, and calcium manganese oxide, indicating that the lime and calcium hydroxide phases had completely dissolved. Cubical particles visible on the steel converter slag particles before dissolution by SEM analysis could not be found from the residual slag, confirming the dissolution of the lime and calcium hydroxide phases (Figure 15). Since the molar ratio of acetic acid and calcium in the slag was the same as in the experiment where calcium leached selectively (0.66 mol CH_3COOH/mol of Ca, i.e., ~200 g slag/mol of CH_3COOH), it seems that, by using a weak acetic acid solution, the lime and calcium hydroxide phases can be selectively dissolved from the steel converter slag, forming a calcium acetate solution.

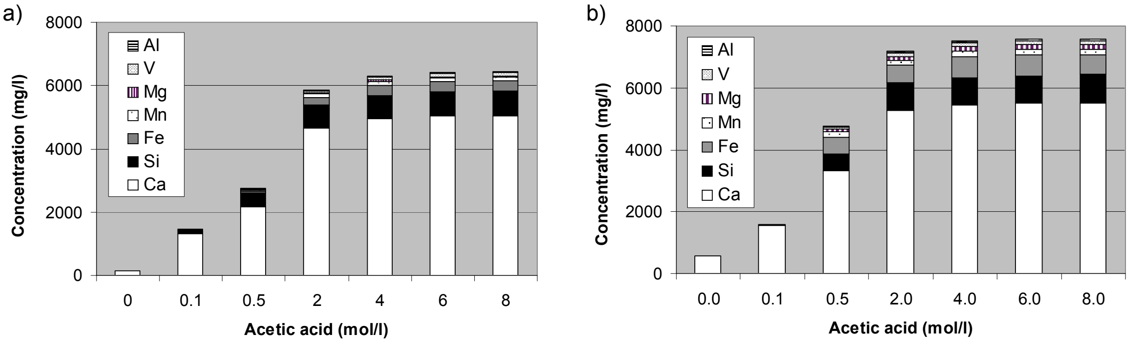

Figure 14. Dissolution of the selected elements from the steel converter slag (10 g) in various concentrations of acetic acid (500 ml) at 30 °C a) two minutes and b) two hours after the slag was added (Eloneva, 2008).

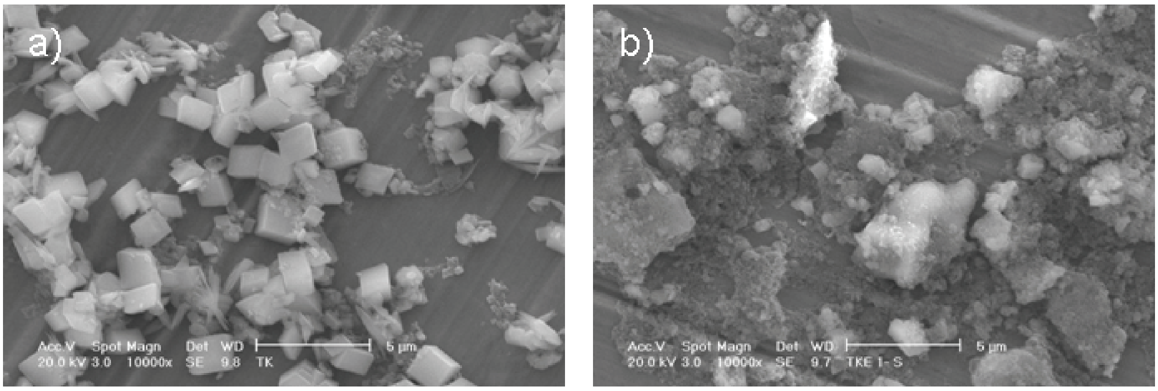

Figure 15. SEM analyses of the steel converter slag (300 g) a) before and b) after dissolution in acetic acid solution (1.5 l, 1 M) at 30 °C (Paper III).

4.2 CO_2 sequestration by precipitation of $CaCO_3$

4.2.1 Description of the experiments

Various experiments were performed to investigate the possibility of fixing CO_2 by precipitating calcium carbonate from the solution of dissolved steelmaking slag and acetic acid (Figure 16). The solutions for these calcium carbonate precipitation experiments were prepared by dissolving the blast furnace slag or steel converter slag in acetic acid solution using methods similar to those described in Chapter 4.1. The dissolution conditions (Table 5) were chosen on the basis of the results from the dissolution experiments (Chapter 4.1). Two hours after the slag was added, the residual slag was removed from the solution by sedimentation and filtration. This was repeated a number of times to produce enough solution for the precipitation experiments.

Since a surplus of acetic acid was used for dissolving the blast furnace slag, the solution that was formed was acidic (pH ~ 4). In the process route proposed by Kakizawa et al. (2001), calcium carbonate is precipitated from a solution of calcium acetate (Equation 16). Calcium acetate is a weak basic salt. Therefore, the excess acid was evaporated from these solutions produced from blast furnace slag (at 150-160 °C overnight). The resulting solid acetate salt precipitates were weighted and analyzed by XRD, XRF, and Total Carbon analysis (TC). Batches of these precipitates were then dissolved in distilled water to produce solutions containing calcium acetate for the precipitation experiments. More detailed descriptions of the solution preparations for the blast furnace slag-based precipitation experiments are presented in Paper II.

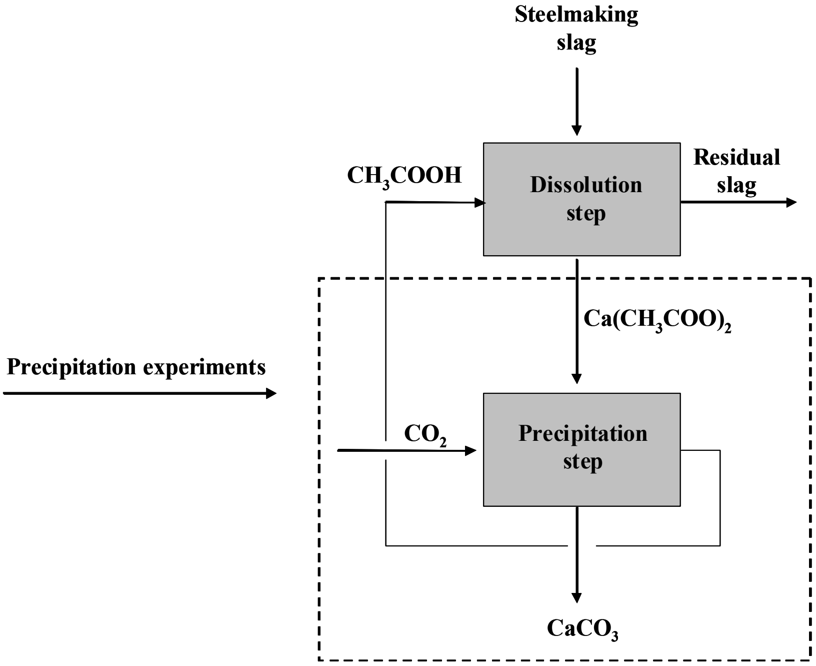

Figure 16. Process step in the acetic acid process route studied in the precipitation experiments (marked with dashed line) (Eloneva, 2008).

Table 5. Parameters of solution preparations for precipitation experiments (Eloneva, 2008).

Steelmaking slag (type)	Mass of the steelmaking slag (g)	Solution (l)	Acetic acid (mol/l)	Solution temperature (°C)
Blast furnace slag	50	1	3.5	70
Steel converter slag	300	1.5	1	30

Solution samples were taken from the solutions derived from steel converter slag for Ca analysis; Fe, Si, Mg, Mn, Al, and V concentrations were analyzed from one of these solutions. The analyses were performed with ICP-AES. More detailed descriptions of the preparation of the solutions for the precipitation experiments based on steel converter slag are presented in Paper III.

In the first precipitation experiment series based on blast furnace slag, the effect of the solution pH and solution temperature on the precipitation of calcium carbonate (from a calcium acetate solution derived from blast furnace slag) was tested. A similar test facility to that described in Chapter 4.1.1 was used. Nitrogen was bubbled through the calcium acetate-containing solution at atmospheric pressure until the solution temperature had stabilized at the desired temperature. When the nitrogen flow was switched off, a carbon dioxide gas flow was switched on. Once the pH and temperature of the solution had stabilized, a specific amount of sodium hydroxide solution was introduced into the solution. NaOH was chosen as a common strong base guaranteeing higher pH conditions. After a constant stabilization time (2 h 15 min), the carbon dioxide flow was switched off and the solution was filtered. The filtered precipitate was washed using distilled water to remove any water-soluble compounds (e.g., sodium hydroxide, sodium carbonate, calcium acetate). The precipitate was then dried at ~120 °C overnight, after which it was analyzed using XRD, TC, and XRF.

As Kakizawa et al. (2001) achieved the best precipitation efficiency at a carbon dioxide pressure of 30 bar, two additional precipitation experiments were performed at 30 bar (± 1 bar), one with NaOH and one without. The experimental set-up used for these experiments contained a batch reactor with a volume of 250 ml and a maximum allowed total pressure of 40 bar (Figure 17). The reactor was heated using a temperature-controlled closed water bath connected to the copper coil surrounding the reactor. The total pressure of the reactor was monitored with a mechanical pressure gauge. The reactor was connected to a nitrogen bottle and a carbon dioxide bottle supplying pressurized gas. The pressure in the reactor was kept constant by keeping the gas inlet valve set to the chosen pressure. The parameters of the blast furnace slag-based precipitation experiments are shown in Table 6, while more detailed descriptions of the experiments are presented in Paper II.

Figure 17. Photo of the test facility used for experiments performed at elevated pressures (Eloneva, 2008).

The steel converter slag-based precipitation experiment series was performed by adding a specific amount of an aqueous NaOH solution into the prepared calcium acetate-containing solution prior to heating and allowing carbon dioxide to flow until the pH of the solution had stabilized. Thus, the stabilization time of the solution pH (i.e. the reaction time of the carbonation step) could be approximated. The effects of the solution temperature, carbon dioxide flow, and gas composition were also tested. The precipitates were analyzed by XRD, XRF, and SEM. The parameters of these experiments are presented in Table 6. One of the experiments was scaled up in order to obtain enough material to measure the ISO brightness and the particle size distribution of the precipitate. The particle size distribution was measured with a laser particle size analyzer (Micrometrics Saturn DigiSizer 5100), while the ISO brightness was measured using an L&W Elrepho SE070 (Lorenz & Wettre). More detailed descriptions of the steel converter slag-based precipitation experiments are presented in Paper III.

Table 6. Parameters of precipitation experiments (Eloneva, 2008).

Steelmaking slag used to prepare the calcium acetate solution	Calcium acetate solution (l)	Solution temperature (°C)	Pressure	NaOH (50 wt-%) (ml)	Gas flow[+] (l/min)	CO_2 (vol-% of the flow)	Time (min)
Blast furnace slag	0.20	30	Atmospheric	0, 2, 5, 20	1	100	135
Blast furnace slag	0.20	50, 70	Atmospheric	0, 5	1	100	135
Blast furnace slag	0.10	50	30 bar CO_2	0, 5	1	100	120
Steel converter slag	1	30 - 70	Atmospheric	0	4	100	120
Steel converter slag	0.25	30	Atmospheric	5, 10, 15, 20	1	100	Until pH stabilized[*]
Steel converter slag	0.25	70	Atmospheric	5	1	100	Until pH stabilized[*]
Steel converter slag	0.25	30	Atmospheric	10	2	10, 25, 50, 100	Until pH stabilized[*]
Steel converter slag	0.25	30	Atmospheric	10	0.5, 1, 2	100	Until pH stabilized[*]

[+] Gas flow of nitrogen and carbon dioxide.

[*] Varied between 14 and 71 minutes.

In order to understand if the acetic acid-based steelmaking slag carbonation is restricted by thermodynamics, thermodynamic equilibrium calculations were performed. The thermodynamic equilibrium calculations were carried out using Outokumpu HSC 5.11 (Roine, 2002), which is a software program based on the minimization of the Gibbs free energy. The program calculates the multiphase chemical reaction equilibrium for ideal solutions, and should therefore give a qualitative indication of the maximum precipitation yield of calcium carbonate from the calcium acetate solution.

4.2.2 Parameters affecting yield and stabilization time

Solid acetate salts produced from the blast furnace slag contained not only calcium acetate hydrates, but also magnesium acetate, according to the XRD analyses (Paper II). The XRF analyses confirmed that the calcium contents were quite high (27-28 wt-% CaO), although the magnesium content was significant as well (7 wt-% MgO). These solids are henceforth referred to as "calcium acetates" and the solutions prepared from them as "solutions of calcium acetate".

The pH of the solution had a clear effect on the precipitation of calcium carbonate from a solution of calcium acetate derived from blast furnace slag (Figure 18): the yield increased as the amount of NaOH (and thus the pH of the solution) was increased to about 20 g of NaOH/l (pH ~ 12) (10 g Ca/l), after which the increase in the yield was insignificant. At higher solution temperatures (50 and 70 °C), the precipitated amounts were similar to those at a solution temperature of 30 °C, indicating that the solution temperature does not have any effect on the yield (at least within the temperature range of 30-70 °C). The higher precipitate yield from the experiment at 30 bar (50 °C) is explained by the higher initial calcium concentration of the calcium acetate solution (20 g Ca/l)[2]. These results indicate that in these conditions (30-70 °C, 1-30 bar, 10 g Ca/l), the maximum calcium carbonate precipitation yield is ~20 g/l and the amount of NaOH required is somewhat above 20 g/l.

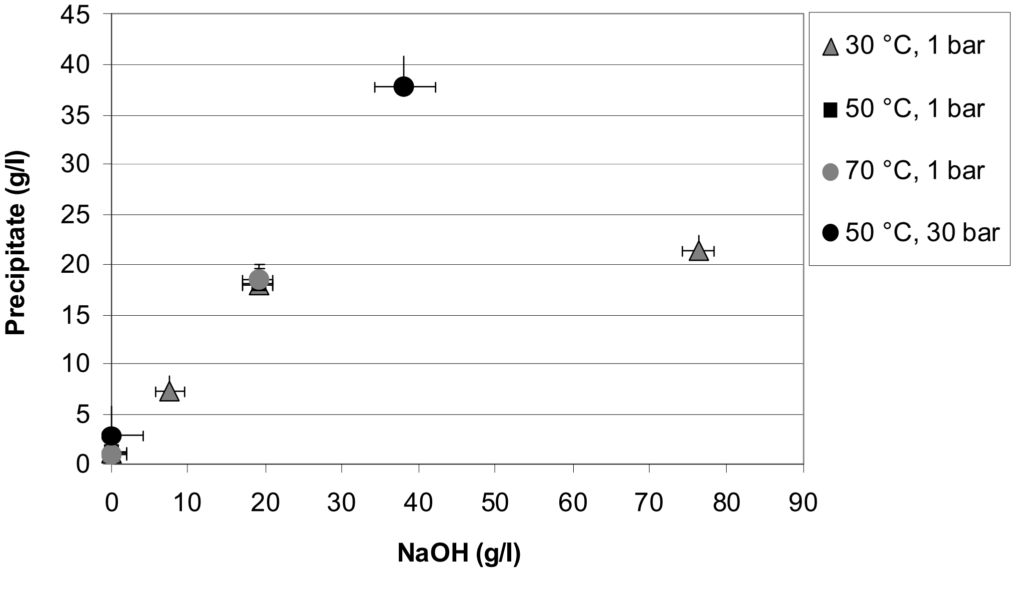

Figure 18. Amount of precipitate formed in relation to amount of NaOH used in the blast furnace slag-based precipitation experiments. (Calcium concentration 10 g/l in solutions of calcium acetate used in experiments performed at 1 bar and 20 g/l at 30 bar) (Paper II).

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[2] The mass of calcium (g) as well as the mass of precipitate formed (g) in the experiments made at elevated pressures are equal to those of the atmospheric experiments with the same NaOH amount (g), the difference in Figure 18 is caused by the different solution volumes (l).

Although the initial pH of the calcium acetate solution prepared from acetic acid and steel converter slag was quite high (pH ~ 11), the mass of the precipitate formed without any sodium hydroxide addition was only 3% of the stochiometric calcium carbonate yield possible with the solution (18.5 g Ca/l) (Paper III). The amount of precipitate enhanced as the amount of NaOH was increased to slightly above 40 g per liter of calcium acetate solution (21.5 g Ca/l) (Figure 19). The solution temperature, carbon dioxide concentration, and carbon dioxide flow rate did not affect the amount of precipitate formed.

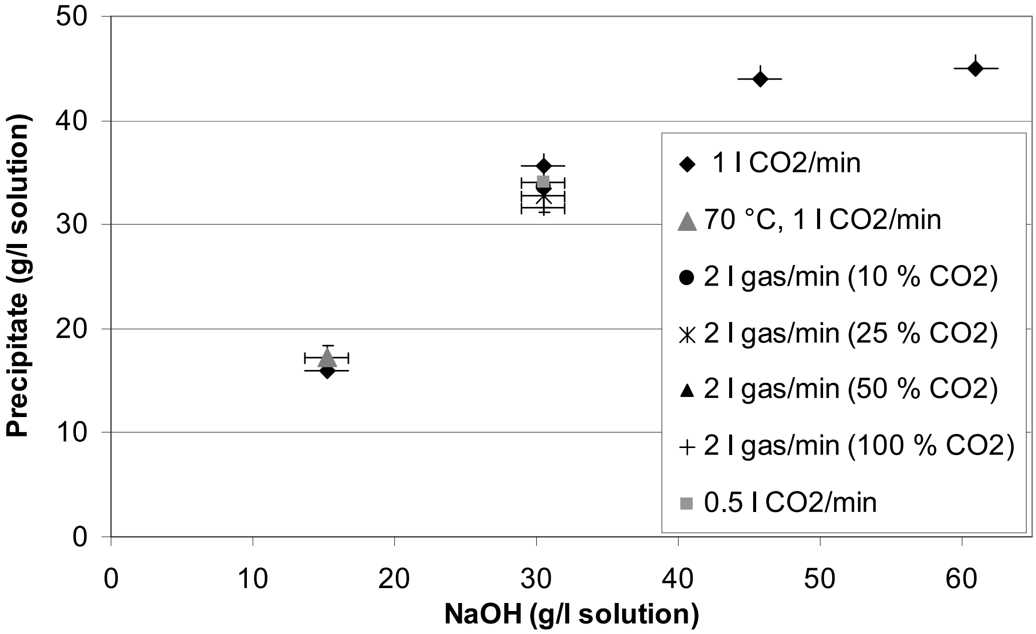

Figure 19. Amount of precipitate formed in relation to amount of sodium hydroxide used in the steel converter slag-based precipitation experiments at 30 °C. (The "triangle"-shaped marker (70 °C, 1 l CO_2/min) represents results from the experiments performed at 70 °C) (Eloneva, 2008).

When sodium hydroxide is not used, acetic acid is, apparently, produced simultaneously with calcium carbonate (Equation 16). This acid is likely to prevent most of the calcium from precipitating as calcium carbonate, i.e., the reaction stops going from left to right. The added NaOH probably reacts with the calcium acetate to form sodium acetate and calcium hydroxide (Equation 31), which produces calcium carbonate when reacting with carbon dioxide (Equation 26). When the molar amount of NaOH is twice or more the molar amount of calcium acetate (i.e., above 43 g NaOH/l calcium acetate solution prepared from steel converter slag), there is no calcium acetate left to produce acetic acid, so calcium carbonate can easily precipitate.

$$Ca^{2+}(aq) + 2CH_3COO^-(aq) + H_2O(l) + CO_2(g) \rightarrow CaCO_3(s) + 2CH_3COOH(aq) \quad (16)$$

$$Ca(CH_3COO)_2(aq) + 2NaOH(aq) \rightarrow 2CH_3COONa(aq) + Ca(OH)_2(aq) \quad (31)$$

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l) \quad (26)$$

The time required for the pH of the solution to stabilize was clearly dependent on the amount of sodium hydroxide used, the solution temperature, the carbon dioxide flow rate, and the carbon dioxide gas concentration (Figure 20). The shortest stabilization times were obtained with the highest solution temperature, carbon dioxide flow rate, and carbon dioxide gas concentration, as well as with the smallest amount of sodium hydroxide.

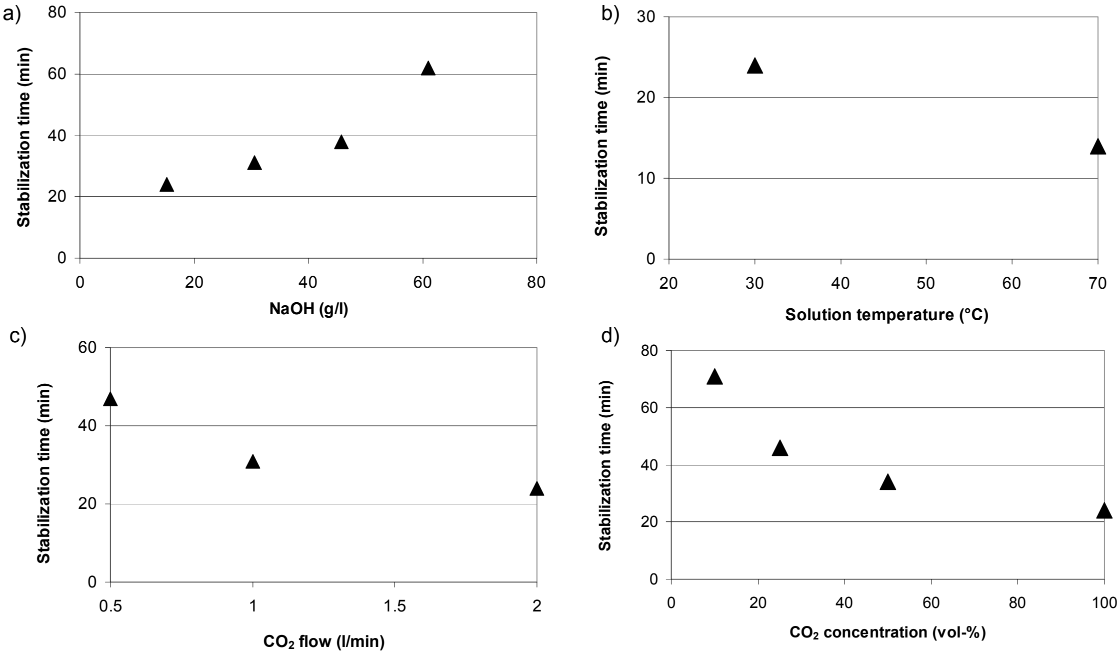

Figure 20. Effect of a) addition of sodium hydroxide b) solution temperature c) CO_2 flow rate and d) CO_2 concentration on the stabilization time of the pH of the solution (Eloneva, 2008).

The conversion of calcium from the calcium acetate solution prepared from acetic acid and steel converter slag into the formed precipitate was calculated on the basis of XRF analyses of the precipitates and ICP-AES analyses of the calcium acetate solution. Depending on the amount of sodium hydroxide used (15-61 g NaOH/l calcium acetate solution), the calcium conversion was 31-86%. On the basis of XRF analyses of the calcium acetates derived from blast furnace slag and the precipitates formed, the calcium conversion from the calcium acetate into the precipitates was calculated to be 19-74% with 8-76 g NaOH/l solution of calcium acetate respectively (Paper II).

4.2.3 Quality of the precipitate

According to the XRD analyses (Table 7), the precipitates formed from the calcium acetate solution (derived from the blast furnace slag) without the addition of any sodium hydroxide were mainly amorphous (Paper II). Even if the former precipitates had been pure calcium carbonate, the calcium conversion from the calcium acetate solution would have been 6% at maximum. However, the calcium conversion at a pressure of 30 bar would agree with the results of Kakizawa et al. (2001). Nevertheless, the precipitation of calcium carbonate seems to be inadequate under these conditions without the addition of sodium hydroxide.

Table 7. Phases in the precipitates formed without addition of any NaOH identified by XRD (Paper II).

Temperature (°C)	Pressure (bar)	Phases identified (in descending apparent order of magnitude)
30	1	Amorphous crystal structure, traces of quartz (SiO_2) and bohmite ($Al_2O_3 \cdot H_2O$)
50	1	Amorphous crystal structure, traces of quartz (SiO_2) and aluminum oxide hydroxide (AlO(OH))
70	1	Amorphous crystal structure, traces of quartz (SiO_2) and calcite ($CaCO_3$)
50	30	Amorphous crystal structure

All the precipitates formed from the calcium acetate solution (derived from blast furnace slag) by adding sodium hydroxide contained calcium carbonates, according to XRD analyses. Carbon dioxide was bound not only as calcite and aragonite, but also as calcite magnesium, which contains a small fraction of magnesium. By assuming that all the calcium oxide was bound as calcium carbonate, the calcium carbonate content of the precipitates was calculated to be ~ 63-89 wt-% (±1%-unit). The purity of commercially available precipitated calcium carbonate (PCC) is typically higher than 97% (Imppola, 2000), indicating that the calcium carbonate produced by this method without additional purification is not suitable for use as PCC. Additionally, the color of the precipitates was not as white as that of the precipitates formed from the calcium acetate solution derived from steel converter slag (Figure 21).

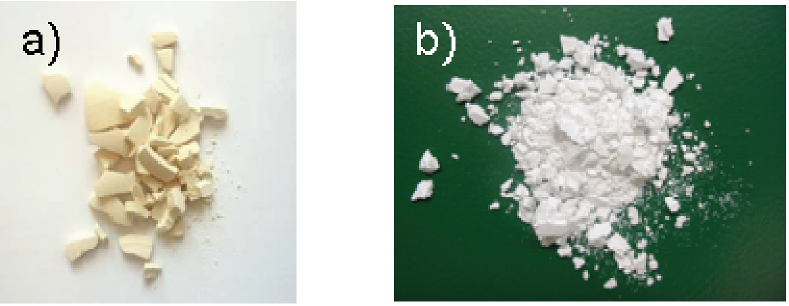

Figure 21. Photos of the precipitates formed with the addition of sodium hydroxide from the calcium acetate solutions derived from a) blast furnace slag and b) steel converter slag.

According to XRD and SEM analyses, the precipitates formed from the calcium acetate solution (derived from steel converter slag) by adding sodium hydroxide were calcium carbonate in the form of calcite with a rhombohedral particle shape (Paper III). The calcite content of the precipitates was calculated to be close to 100 wt-%. The particles of the precipitate formed without the addition of any NaOH had the shape of aragonite. It is possible that this was a result of a higher solution temperature (~ 60 °C). The solution temperature was increased during the precipitation experiment, because the color of the solution at 30 °C (without the addition of any NaOH) indicated that no precipitation was occurring. The particle sizes of the precipitate produced at 70 °C with 15 g NaOH/l calcium acetate solution were significantly larger and had a more complex form than those at 30 °C. Interestingly, the particles of the precipitates from the experiments where 31 g NaOH/l calcium acetate solution was used were slightly smaller than those produced with 15, 46, or 61 g NaOH/l calcium acetate solution at 30 °C. These results indicate that the shape and size of the particles are affected both by the solution temperature and the amount of sodium hydroxide added.

The ISO brightness of the precipitate formed in the scaled-up experiment using 46 g NaOH/l calcium acetate solution was very high (98.7%). The particle size distribution was 0.1-4 µm for 96 vol-% of the particles with a mean value of 0.6 µm and a mode value of 0.3 µm. Evidently, calcite precipitating from the solution of dissolved steel converter slag and acetic acid with the help of sodium hydroxide at a low temperature (~ 30 °C) has a rhombohedral particle shape, very high brightness, and small particle size.

4.2.4 Thermodynamic calculations

The thermodynamic calculations that were performed showed that the addition of sodium hydroxide should have a clearly more pronounced effect on the calcium carbonate conversion than the temperature, pressure, and calcium concentration (Figure 22) (Paper II[3]). The gap between the experimentally found conversions and thermodynamically calculated conversions was 21-30%-units and 3-14%-units for the cases where sodium hydroxide was used for the carbonation based on blast furnace slag and steel converter slag, respectively.

The thermodynamic calculations predicted a calcium conversion of 4% at atmospheric pressure and 22% at 30 bar when no sodium hydroxide is used. The experiments performed under similar conditions with the blast furnace slag did not result in any detectable amount of precipitated carbonate, but, at atmospheric pressure, the calcium conversion was 3% for the steel converter slag-based carbonation. While it is possible that amorphous carbonate was formed in the former case, although XRD did not detect any carbonate phases, the gap between the experimentally found conversions and thermodynamically calculated conversions at 30 bar is at least 16%-units.

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[3] Calculations are based on the data in the Paper II with aid of additional data.

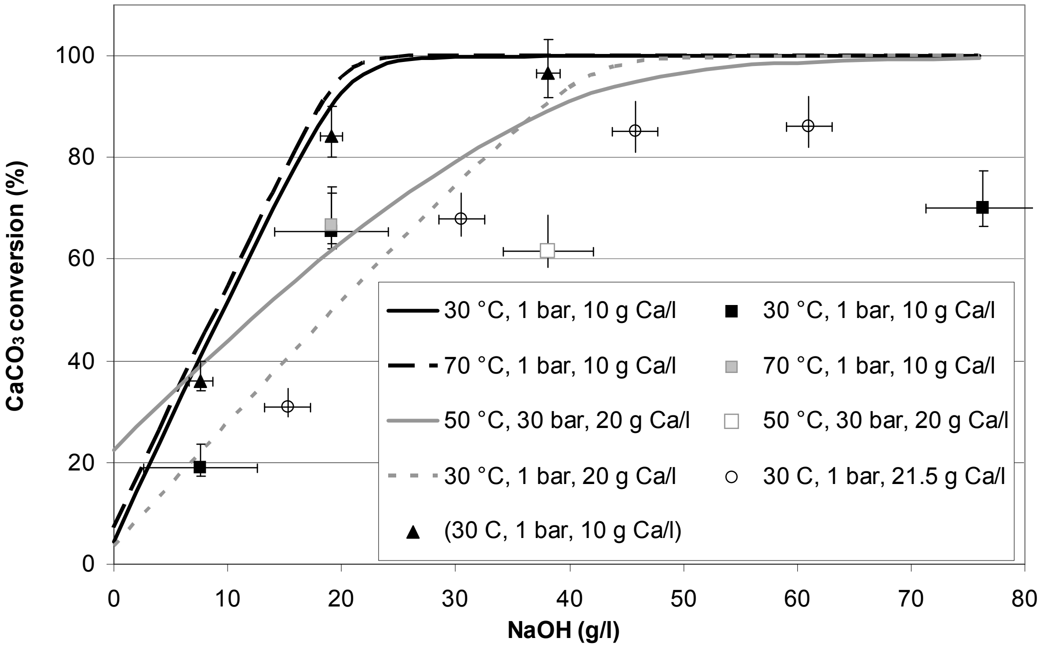

Figure 22. Calcium carbonate conversion from a solution of calcium acetate under various conditions based on thermodynamic calculations compared to the results from the experiments with blast furnace slag and steel converter slag-derived calcium acetate solutions. The "square"-shaped markers represent results from the experiments with blast furnace slag, while the "ring"-shaped marker represents steel converter slag-based experiments and the "triangle"-shaped marker (30 °C, 1 bar, 10 g Ca/l) represents results from the experiments with chemical purity calcium acetate (94 wt-%). Lines represent results from the thermodynamic calculations (Eloneva, 2008).

The thermodynamic calculations were based on a pure calcium acetate solution, while the experiments were performed with calcium acetate solution produced from blast furnace slag or steel converter slag. Therefore, part of the difference between the results of the modeling and the experiments (especially with blast furnace slag) can be explained by the precipitation of other compounds (containing elements such as magnesium, iron, silica, and aluminum), which were not included in the model. This was verified by a series of experiments (30 °C, 1 bar, 10 g Ca/l) with commercial-grade calcium acetate (94 wt-%, manufactured by Riedel-de Haën), which reduced the gap between the experimental and modeling results significantly. Since the pH of the calcium acetate solutions had clearly stabilized before the experiments were finished, it seems unlikely that a longer reaction time would have improved precipitation, indicating that the precipitation of calcium carbonate in these conditions is controlled by thermodynamics.

4.3 Feasibility analysis

The feasibility of the acetic acid-based steelmaking slag carbonation as a CO_2 sequestration and calcium carbonate production method was studied by calculating the costs of the chemical consumption of the methods, as well as the heat required for the evaporation of the acetic acid for the production of solid calcium acetate salt from blast furnace slag.

The weakest acetic acid solution dissolved about 25-30% of the calcium in the steel converter slag (100 g slag/mol CH_3COOH), while the calcium conversion from the solution into the ~100 wt-% pure calcium carbonate precipitate was 31-86% (Paper III). It can, then, be roughly calculated that the production of 1 t of pure calcium carbonate would, in the best case, consume 4.8 t of steel converter slag, 1.4 t of acetic acid, and 0.9 t of sodium hydroxide, and produce 1.9 t of sodium acetate (Figure 23). Simultaneously, 440 kg of carbon dioxide would be fixed in the stable form of a carbonate. In Finland, the price of sodium hydroxide is ~ €400/t, the price of acetic acid ~ €2070/t, and the price of sodium acetate is ~ €680/t (Algol Chemicals Oy, 2007). This means that the chemical costs of producing pure calcium carbonate by using this method would be as much as €1990/t, assuming that the sodium acetate produced in the process could be sold for €680/t.

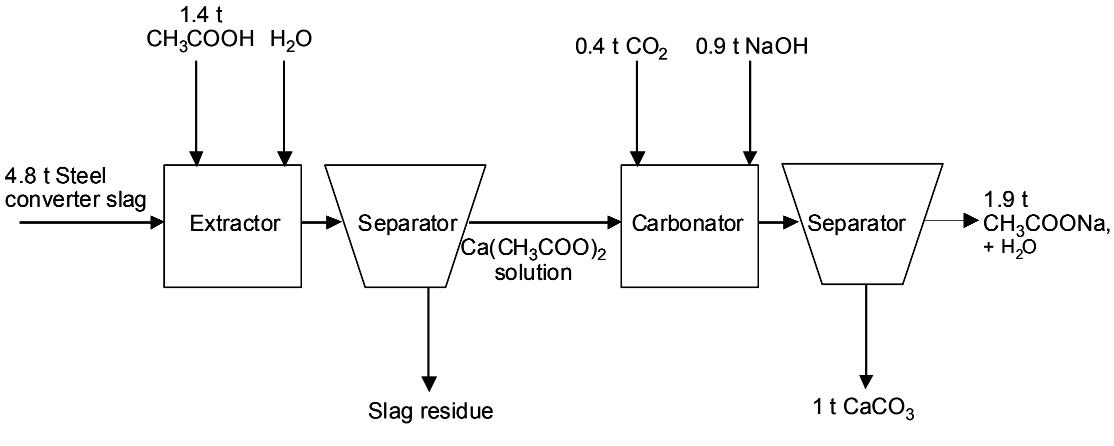

Figure 23. A simplified process scheme for producing 1 t of pure $CaCO_3$ from steel converter slag via the acetic acid route.

Thermodynamic equilibrium calculations showed that adding ~28 g NaOH per liter of blast furnace slag-derived calcium acetate solution (10 g Ca/l) is the point where the precipitation of calcium carbonate reaches its limit (at 30 °C, 1 bar) (Paper II). With this amount of NaOH, about 20 g of 90 wt-% pure calcium carbonate should precipitate per liter of calcium acetate solution produced from the blast furnace slag, binding ~ 8 g CO_2. This means that, in order to bind 1 kg of carbon dioxide, 126 l of prepared calcium acetate solution is needed with 3.5 kg of NaOH, producing ~ 2.5 kg of 90 wt-% pure $CaCO_3$ (Figure 24). The production of this calcium acetate solution would consume approximately 4.4 kg of the slag and 27 kg of acetic acid (10 g slag/mol CH_3COOH), of which a large part (~ 24 kg acetic acid) could be relatively easily recycled by evaporation and condensation.

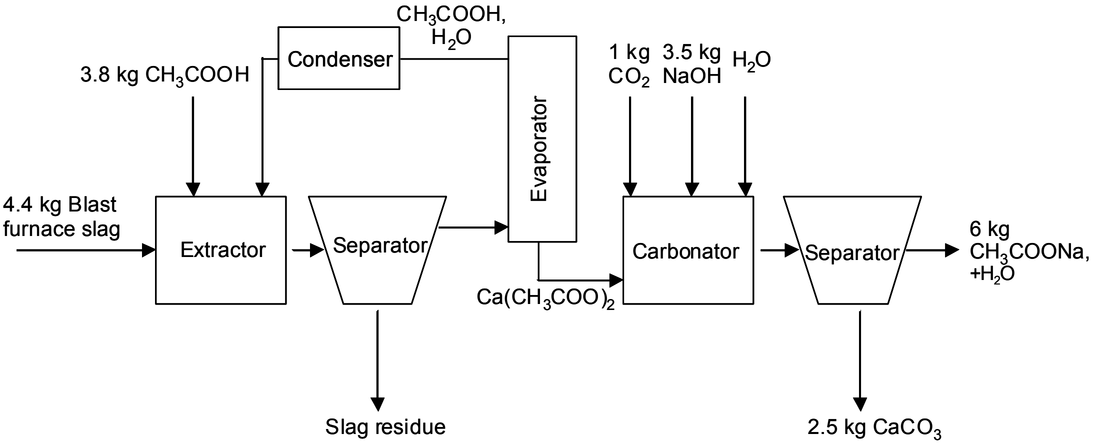

Figure 24. A simplified process scheme for binding 1 kg of carbon dioxide by carbonating acetate produced from blast furnace slag.

The heating of the raw materials (up to 70 °C) and dissolution of the blast furnace slag (the calculations were based on wollastonite, which resembles blast furnace slag) in acetic acid (50 wt-%) require 1 MJ of heat per kilogram of slag. With a stronger acetic acid solution, the heat requirement is reduced (~ 9 kJ/kg of slag with a 100 wt-% acetic acid solution). The evaporation temperature for the excess acid (22.5 l) was set to 120 °C, i.e., slightly above the boiling point of pure acetic acid (118 °C). Assuming that the released vapor consists of steam and acetic acid gas, the heat requirement of the evaporation step would be 1-2 MJ per l of acetic acid solution evaporated, depending on the concentration of the acetic acid. Since neither temperature nor pressure was found to have any significant effect on the carbonation process, the carbonation could be carried out at 30 °C and a carbon dioxide pressure of 1 bar (i.e., no need for reactor pressurization). The precipitation of calcium carbonate would produce 2 MJ of heat per kilogram of carbon dioxide fixed.

The carbon dioxide emission factor for coal is 94.6 g/MJ (Statistics Finland, 2009). Therefore, carbon dioxide emissions from the heat generation would be from 2 to 8 times the amount of carbon dioxide stored by the carbonation step (with 100 wt-% and 50 wt-% acetic acid solutions, respectively). The carbon dioxide emissions would be even higher if a weaker acetic acid concentration was used. The temperature required for the evaporation step is quite low, and it is very likely that some of the heat required could be acquired by process integration using waste heat from the steelmaking plant itself. However, while the evaporated acetic acid solution could be condensed and sent back to the dissolution reactor, the acetic acid bound as calcium acetate, as well as the sodium hydroxide used, would need to be purchased or regenerated. The consumption of these chemicals would cost about €9300/t CO_2 fixed as $CaCO_3$.

4.4 Evaluation of the acetic acid process route

The focus of this chapter was on studying the suitability of the acetic acid process route, suggested by Kakizawa et al. (2001), to fix CO_2 as pure calcium carbonate with steelmaking slags as the calcium-containing raw material. According to the experiments, acetic acid dissolved calcium efficiently from both the blast furnace slag and the steel converter slag. Complete and rapid dissolution of the blast furnace slag was achieved with strong acetic acid solutions containing at least one mol of CH_3COOH per 10 g of slag. The dissolution of the steel converter slag was also rapid, although, unlike with the blast furnace slag, 100% calcium extraction was not reached. Those solutions that were able to dissolve calcium efficiently dissolved significant amounts of other measured elements too, such as Al and Mg from the blast furnace slag and Fe and Si from the steel converter slag. This is undesirable, because a commercial calcium carbonate product should contain as few impurities as possible.

A weak acetic acid solution (containing 1 mol of CH_3COOH/200 g slag) was found to dissolve only lime and calcium hydroxide from the steel converter slag, forming a solution that contains mostly calcium acetate. Only 2% of the calcium dissolved from the blast furnace slag with the weakest acetic acid solution, while stronger solutions dissolved some part of the other measured elements as well. It is possible that solutions containing clearly less acid than these stronger solutions, but more than the weakest solution used, would also have dissolved calcium selectively from the blast furnace slag. However, this is unlikely, because blast furnace slag does not contain free lime as steel converter slag does.

The solution temperature had a clear effect on the dissolution of calcium from the blast furnace slag, while the dissolution of the steel converter slag was quite similar at all solution temperatures tested. The highest calcium extraction efficiency for the blast furnace slag was reached at the lowest solution temperature (30 °C), although the dissolution was somewhat slower than at 50 or 70 °C. Evidently, the higher the temperature, the higher the rate of dissolution; however, the solubility of calcium decreases as the temperature increases. A longer leaching time was found to promote the formation of silica gel, which is generally unwanted as it could create problems with the process equipment e.g. by preventing efficient filtration.

Precipitation experiments were carried out with a solution of calcium acetate produced by using acetic acid to dissolve blast furnace slag or steel converter slag. It was found that efficient calcium carbonate precipitation requires significant additions of NaOH to increase the alkalinity of the solution, as well as to prevent the formation of acid during carbonation. The temperature of the solution (30-70 °C), pressure (1-30 bar), gas flow rate, or carbon dioxide concentration did not have any significant effect on the precipitation yield. On the basis of these results, it is likely that flue gases could be used as a source of carbon dioxide without the need for energy-intensive separation of CO_2 from the flue gas. The possible longer precipitation time needed, caused by the low carbon dioxide concentration in flue gases (which was indicated by the longer stabilization time for the pH of the solution), could be compensated for by an increase in the solution temperature or gas flow.

The calcium carbonate (calcite, aragonite, calcite magnesium) content of the precipitates produced from the blast furnace slag with the addition of NaOH was calculated to be ~ 60-90 wt-%. The stepwise addition of NaOH could probably have been used for the removal of iron prior to carbonation in the same way as in the process route proposed and studied by Park and Fan (2004 and 2005). However, as calcium carbonates produced from the steel converter slag by using the addition of NaOH had a significantly higher purity (close to 100 wt-%) and whiter color than those produced from the blast furnace slag, it is quite clear that a selective dissolution of calcium is required for the production of high-purity calcium carbonate from steelmaking slags.

Preliminary process calculations for the acetic acid-based carbonation method with blast furnace slag as the calcium-containing raw material showed that approximately 4.4 kg of blast furnace slag, 3.8 kg of acetic acid, and 3.5 kg of sodium hydroxide would be required to bind 1 kg of carbon dioxide by this method, resulting in 2.5 kg of 90 wt-% calcium carbonate. The production of energy required to evaporate the acetic acid was calculated to generate more carbon dioxide than would be bound by the carbonation step. Although the heat needed for the evaporation of the acetic acid could probably be acquired as waste heat by the integration of the process with other processes, the costs of the chemicals consumed would make the process clearly too expensive for CO_2 sequestration.

The calcium carbonates produced from the steel converter slag by using the addition of NaOH were in the form of calcite. It was found that the shape and size of these precipitates is affected both by the solution temperature and the amount of sodium hydroxide added. The precipitate formed at low temperatures by adding sodium hydroxide has a rhombohedral particle shape, very high brightness, and small particle size. The costs of the chemical consumption of this process route were calculated to be €1990 per t of pure calcium carbonate produced, assuming that the sodium acetate produced in the process could be sold for €680/t. Although the particle size of the precipitates was almost small enough for an expensive nano grade PCC (<0.1 µm), the costs related to the consumption of chemicals clearly exceed the price of nano PCC (Roskill, 2008). Since the calcium acetate solution produced from the steel converter slag can be alkaline, the energy-intensive evaporation step can be avoided in this process route. Ideally, this process would consume 440 kg CO_2/t $CaCO_3$ produced, as well as an additional 220 kg of CO_2 per every conventionally produced PCC replaced (Nordkalk Oy, 2006). Unfortunately, the indirect CO_2 emissions from the production of the chemicals consumed in the process would most probably exceed these reductions.

The main obstacle of this process route is the use of sodium hydroxide, which prevents the efficient recycling and re-use of the chemicals. Therefore, the key issue for developing a feasible process for producing pure calcium carbonate from steelmaking slags with negative CO_2 emissions seems to be finding an effective calcium-selective solvent that can be fully recovered and reused.

5 Determination of an alternative process route

In this chapter, an alternative to the acetic acid process route is presented. The selective extraction of calcium from the steelmaking slags is experimentally investigated using various different solvents. The precipitation of calcium carbonate from the formed solution with the help of CO_2 is also experimentally studied. The feasibility of the method based on the most promising solvents is assessed as well. Furthermore, the quality of the residual slag was experimentally investigated.

5.1 Solvent selection studies

5.1.1 Description of the experiments

In order to find a suitable solvent for dissolving calcium selectively from steelmaking slags, various relatively common solvents were tested (Paper IV). The slag (1 g), ground to a specific grain size (74-125 µm), was added to an Erlenmeyer flask containing a particular concentration of a certain solvent (an aqueous solution) (Table 8). Ammonium chloride and ammonium nitrate were selected as solvents on the basis of the promising results by Yogo et al. (2005), while a few other ammonium salts were also included. Aluminum nitrate and aluminum sulphate were selected as they also (like ammonium chloride and ammonium nitrate) give aqueous solutions that are acidic. Acids, including acetic acid, were selected for comparison purposes, while a few relatively common solvents were tested as well. The solutions were stirred at 100 rpm at room temperature and at atmospheric pressure. The solutions were immediately filtered with 0.45-µm Pall GxF syringe filters 1 h after the addition of the slag. The concentrations of Ca, Si, Fe, Mg, Al, Mn, and V were measured in the filtered solutions with ICP-AES. The concentration of Cr[4] was measured with atomic absorption spectrometry (AAS).

The steelmaking slags used in the experiments were the steel converter slag, desulphurization slag, and ladle slag provided by the Raahe Works, as well as blast furnace slag provided by Ovako Koverhar. The slag fractions that were used were analyzed by total digestion and ICP-AES, and samples of the batches were sent for XRD and XRF analysis.

In order to understand if the dissolution of the main calcium silicate phase of the steel converter slag (i.e., larnite) is restricted by thermodynamics, thermodynamic equilibrium calculations were carried out using the Outokumpu HSC 5.11 software (Roine, 2002).

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[4] Cr was analyzed only in the experiments made with steel converter slag and blast furnace slag.

Table 8. Parameters of solvent selection experiments.

Steelmaking slag (type)	Solvents	Solution volume (l)	Concentration (mol/l)
Steel converter slag	CH_3COOH, CH_3CH_2COOH, HNO_3, H_2SO_4, NaCl, CH_3COONa, NH_4Cl, CH_3COONH_4, NH_4NO_3, $(NH_4)_2SO_4$, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $Al_2(SO_4)_3$, $Al(NO_3)_3$, NaOH, $(NH_2)_2CO$	0.050	0.1, 0.2, 0.3, 0.5, 1, 2
Blast furnace slag, Desulphurization slag, Ladle slag	NH_4NO_3, NH_4Cl, CH_3COONH_4	0.050	0, 0.5, 1, 2

5.1.2 Characterization of the slags

The results from the XRF, ICP-AES, and XRD analyses of the slags are listed in Table 9, Table 10, and Table 11 (Paper IV). The sieved fractions were found to represent the batches from which the fractions were taken quite well, although the calcium contents of the desulphurization slag and ladle slag were clearly higher in the batches than in the sieved fractions. In addition, the iron and silica contents of the ladle slag, as well as the silica content of the blast furnace slag, were higher in the batches than in the sieved fractions, while the iron content of the desulphurization slag was lower in the batch than in the sieved fraction.

Table 9. XRF analysis of steel converter slag, blast furnace slag, desulphurization slag, and ladle slag, 0-1 mm (selected components and elements listed, expressed as oxides). Units in wt-%.

Slag type	CaO	FeO	SiO_2	MgO	MnO_2	Al_2O_3	V_2O_3
Steel converter slag	45.9 (±0.7)	21.4 (±0.2)	13.9 (±0.3)	3.7 (±0.1)	3.6 (±0.1)	2.0 (±0.1)	1.44 (±0.06)
Blast furnace slag	34.5 (±0.7)	0.29 (±0.01)	31.2 (±0.8)	16.2 (±0.4)	0.06 (±0.01)	12.7 (±0.3)	0.065 (±0.003)
Desulphurization slag	58.0 (±0.7)	9.0 (±0.2)	15.0 (±0.3)	1.3 (±0.1)	0.54 (±0.05)	2.5 (±0.1)	0.15 (±0.02)
Ladle slag	49.4 (±0.7)	5.6 (±0.2)	14.1 (±0.3)	5.8 (±0.4)	1.2 (±0.1)	21.0 (±0.3)	0.39 (±0.02)

Table 10. ICP-AES analysis of sieved fraction (74-125 µm) of steel converter slag, blast furnace slag, desulphurization slag, and ladle slag (only selected elements measured, expressed as oxides). Units in wt-%.

Slag type	CaO	FeO	SiO_2	MgO	MnO_2	Al_2O_3	V_2O_3	Cr_2O_3
Steel converter slag	42.1	18.5	10.8	4.7	3.5	2.3	1.5	0.2
Blast furnace slag	36.8	0.1	26.6	16.2	0.04	11.2	0.04	<0.01
Desulphurization slag	49.8	14.5	13.1	0.9	0.4	1.8	0.2	-
Ladle slag	42.0	0.4	9.1	6.2	0.2	22.3	0.04	-

Table 11. Phases in the slags (0-1 mm) identified by XRD.

Slag type	Phases identified (in descending apparent order of magnitude)
Steel converter slag	Ca_2SiO_4, Ca_2FeAlO_5, FeO, CaO
Blast furnace slag	$Ca_2(Al(AlSi)O_7)$, $Ca_3Mg(SiO_4)_2$, $CaMgSiO_4$, $Ca_2(Mg_{0.5}Al_{0.5})(Si_{1.5}Al_{0.5}O_7)$
Desulphurization slag	Ca_2SiO_4, CaO, Ca_2FeAlO_5, CaS, Fe_3O_4
Ladle slag	$Ca_3Al_{0.84}Fe_{1.16}Si_3O_{12}$, Ca_2SiO_4, MgO, SiO_2, Fe_3O_4, FeO

5.1.3 Dissolution of calcium from the steel converter slag

The dissolution of calcium from steel converter slag in the solvents that were used in the tests is presented in Figure 25 (Paper IV). Three of the acids (acetic acid, nitric acid, and propionic acid), as well as three of the ammonium salts (ammonium nitrate, ammonium acetate, and ammonium chloride), dissolved calcium efficiently (>50%) from the steel converter slag. 85-100% of the calcium in the slag was dissolved in all these acids when the concentration was greater than 0.5 M, while the ammonium salt solutions with similar concentrations dissolved 50-80% of the calcium. Ammonium nitrate was clearly the most efficient salt solution, dissolving ~10%-units more calcium than ammonium chloride or ammonium acetate. The strongest aluminum nitrate solution (0.2 M) dissolved 45% and the strongest ammonium sulphate solution (2 M) dissolved ~30% of the calcium in the slag, while weaker concentrations, as well as the other solvents that were tested, dissolved less than 20%. Additionally, distilled water dissolved only 10% of the calcium from the steel converter slag.

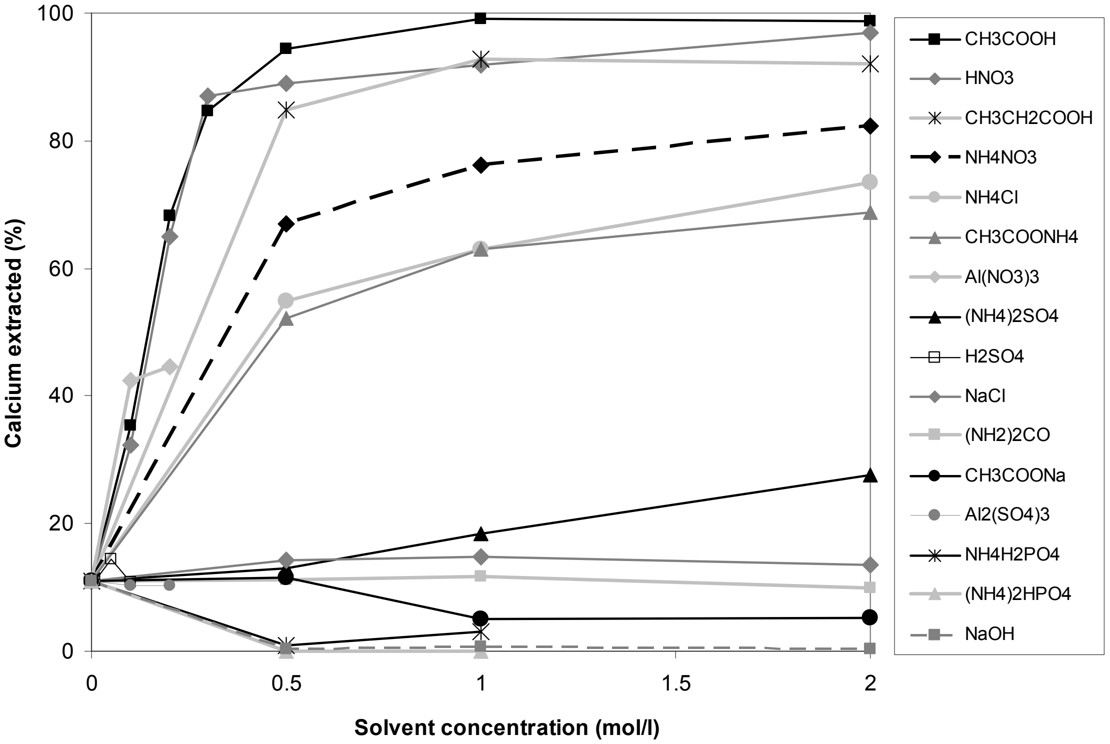

Figure 25. Dissolution of calcium from steel converter slag (1 g) in various concentrations of different solvents (50 ml) at room temperature (Paper IV).

Both ammonium chloride and ammonium nitrate are salts of a weak base and a strong acid, giving aqueous solutions that are acidic. Their ability to dissolve calcium efficiently from the steel converter slag was found to be in quite good agreement with the findings of Yogo et al. (2005) and Kodama et al. (2008). Ammonium acetate is a salt of a weak acid and weak base and its aqueous solution should be neutral (Zumdahl and Zumdahl, 2003). However, it dissolved calcium from the slag almost as efficiently as ammonium nitrate and ammonium chloride did. This indicates that the acidity of the solution is not the only factor affecting the dissolution of calcium from the steel converter slag using these salts. A high solubility of the calcium salt is of great importance. In fact, calcium nitrate (as well as calcium acetate and calcium chloride) has a much higher solubility in water than CaO has as $Ca(OH)_2$ (Fält, 2009).

Besides having the capability to dissolve calcium efficiently from steelmaking slag, the solvent also needs to be selective for calcium to obtain a pure calcium carbonate precipitate from the solution that is produced. When steel converter slag is dissolved in ammonium salt solutions (0.5-2 M) (NH_4NO_3, NH_4Cl, or CH_3COONH_4), calcium seems to be the only element dissolving from the slag in any significant amount (Figure 26) (i.e., besides Ca, among the measured elements only Si was detected by the ICP-AES or AAS). Weak concentrations of acetic acid and nitric acid (0.1 and 0.2 M) also managed to extract calcium almost selectively (Figure 27). However, carbonating such a solution is not feasible, since the acid would regenerate and prevent the efficient precipitation of calcium carbonate. Therefore, ammonium salt solutions (NH_4NO_3, NH_4Cl, and CH_3COONH_4) seem to be the most promising solvents amongst the ones that were tested for dissolving calcium selectively from the steel converter slag prior to carbonation.

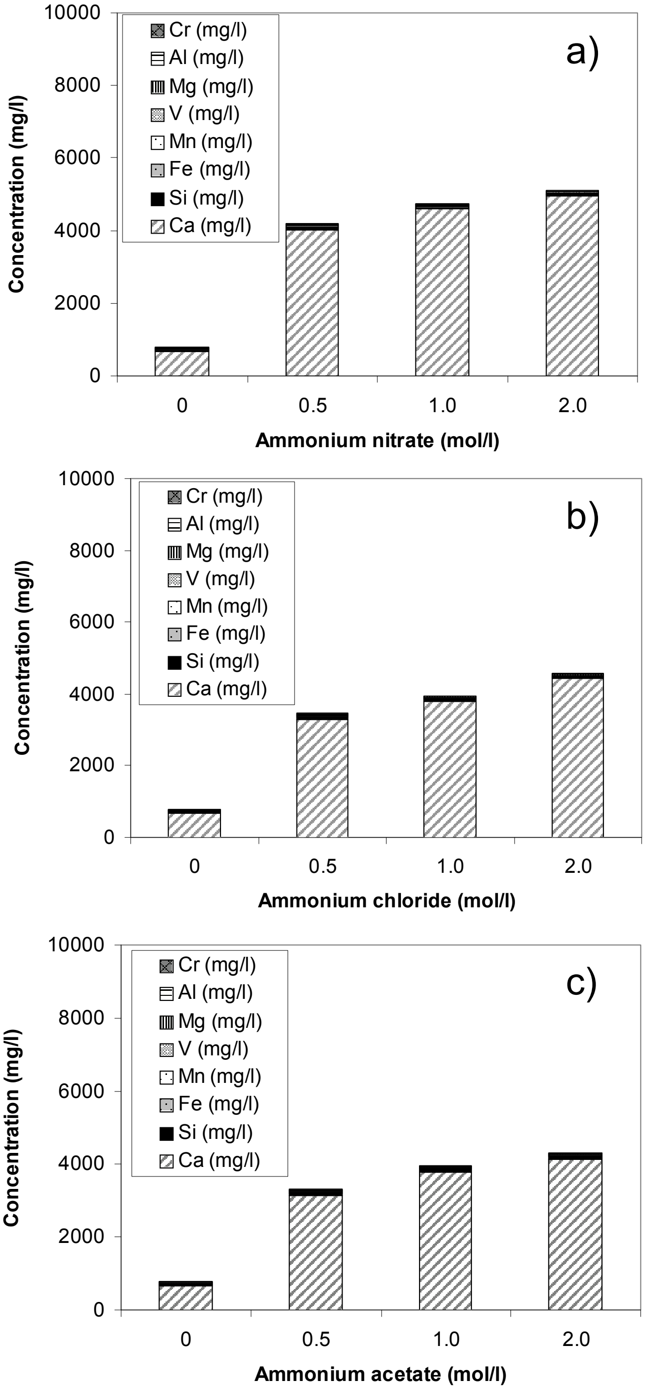

Figure 26. Dissolution of selected elements from steel converter slag (1 g) in various concentrations of aqueous solution of a) ammonium nitrate b) ammonium chloride c) ammonium acetate (50 ml) at room temperature (Paper IV).

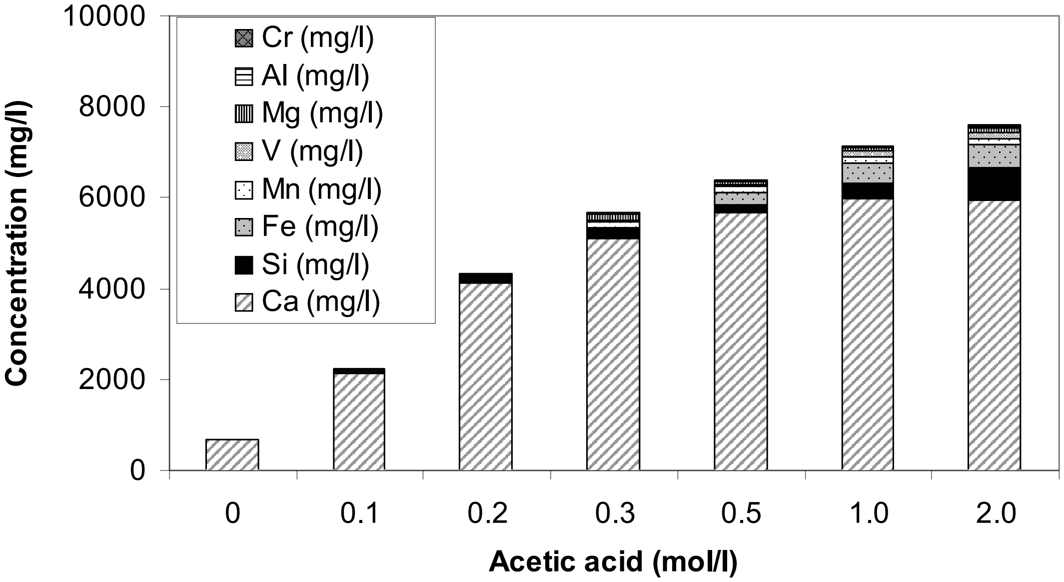

Figure 27. Dissolution of selected elements from steel converter slag (1 g) in various concentrations of aqueous solution of acetic acid (50 ml) at room temperature (Paper IV).

5.1.4 Dissolution of calcium from the other types of slags from the integrated steel manufacturing process

The possibility of using ammonium salt solutions (NH_4NO_3, NH_4Cl, and CH_3COONH_4) to dissolve calcium selectively from blast furnace slag, desulphurization slag, and ladle slag was also investigated (Paper IV). All these solutions dissolved less than 10% of the calcium in blast furnace slag (Figure 28). Calcium also dissolved quite poorly (25% extraction at maximum) from the ladle slag. On the contrary, over 50% of the calcium in desulphurization slag dissolved in aqueous solutions of ammonium nitrate and ammonium acetate. Ammonium acetate was the most efficient ammonium salt solution to dissolve calcium from the desulphurization slag, with a 2 M solution dissolving ~ 70% of the calcium in the slag. While 2 M ammonium chloride also dissolved calcium quite efficiently (~ 50%), only 30% of the calcium was dissolved in the 0.5 and 1 M solutions. All these solvents dissolved calcium quite selectively from the desulphurization slag and ladle slag, but from the blast furnace slag small amounts of magnesium and silica were also dissolved.

According to the results from the XRD analyses, both steel converter slag and desulphurization slag contained free lime, while all of the calcium in the blast furnace slag and ladle slag was bound in silicates. This might partly explain why calcium is efficiently dissolved from the steel converter slag and desulphurization slag, but not from the ladle slag and blast furnace slag. The amount of calcium dissolved from the steel converter slag with ammonium salts (4.1-5.0 g/l) was quite close to that dissolved when a weak concentration of acetic acid (0.2 M) was used (4.1 g/l) (i.e., when calcium dissolved almost selectively from the slag). In fact, in all cases where more than 5 grams of calcium were dissolved per liter of solvent used, some of the other elements were dissolved from the steel converter slag as well.

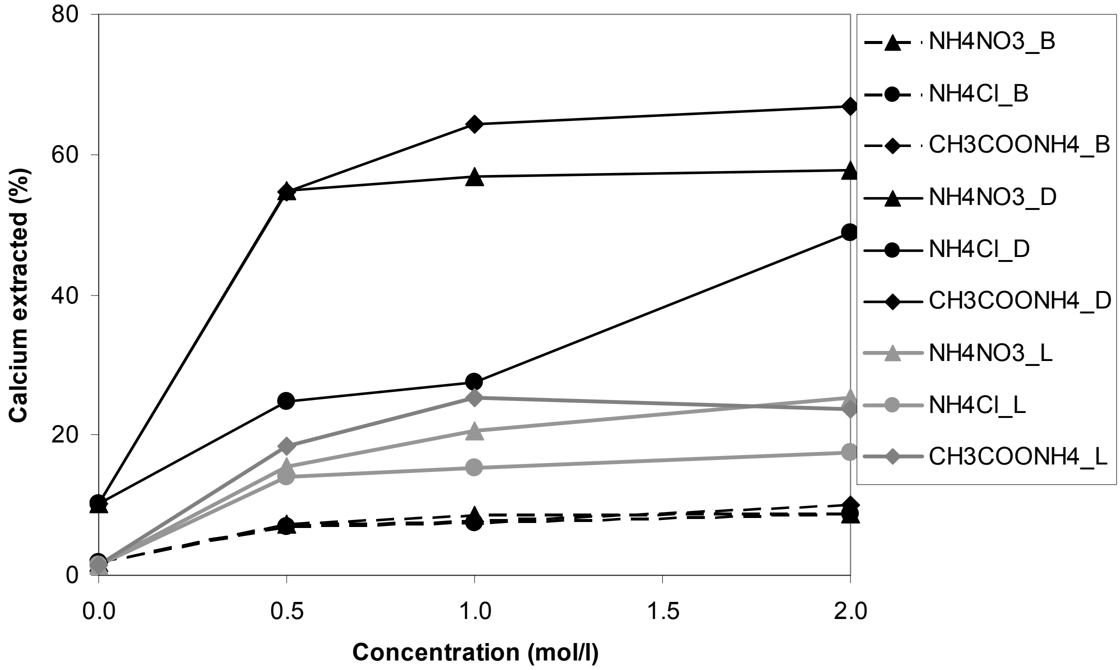

Figure 28. Dissolution of calcium from the blast furnace slag (marked by the letter "B"), from the desulphurization slag (marked by the letter "D"), and from the ladle slag (marked by the letter "L") (1 g) in various concentrations of different solvents (50 ml) at room temperature (Paper IV).

5.1.5 Thermodynamic equilibrium calculations

A few thermodynamic equilibrium calculations were carried out to investigate whether calcium dissolves from the calcium silicates in an aqueous solution of ammonium salt (Paper IV). The equilibrium of the solution was calculated using the Outokumpu HSC 5.11 software (Roine, 2002) for Gibbs energy minimization. Since larnite is one of the main phases in steel converter slag, and is also found in ladle slag and desulphurization slag, it was used to model the calcium silicate phase. Ammonium acetate was chosen to represent the ammonium salt. The thermodynamic equilibrium calculations showed that 50% of the calcium should already be dissolved from Ca_2SiO_4 in water (Table 12). The remaining calcium would be bound as $CaSiO_3$, which starts to dissolve when the CH_3COONH_4 concentration is above 0.2 mol/l. Approximately half of the $CaSiO_3$ is dissolved in a 1 M solution and almost all the calcium is dissolved in a 2 M solution. These results indicate that the dissolution of calcium from larnite (or wollastonite) is not restricted by thermodynamics, provided that sufficient extractive capacity is used. However, these calculations do not take chemical kinetics or mass transfer limitations into account.

Table 12. Thermodynamic equilibrium composition of larnite (20 g) in aqueous solution of ammonium acetate (0-2 mol/l). (Input: 850 g H_2O (l), 0-154 g CH_3COONH_4 (aq), 20 g Ca_2SiO_4 (s), 1 l N_2 (g)) (Paper IV).

In aqueous solution of ammonium acetate (mol/l)	Composition as conversion ratio of Ca (%)			
	$Ca(CH_3COO)_2$ (aq)	$CaSiO_3$	$Ca(OH)_2$	Ca^{2+}
0	0	50	47	3
0.5	45	46	0	9
1	74	22	0	3
2	95	4	0	1

In aqueous solution of ammonium acetate (mol/l)	Composition as conversion ratio of Si (%)	
	$CaSiO_3$	SiO_2
0	100	0
0.5	91	9
1	45	55
2	8	92

5.2 CO_2 fixation by precipitation of $CaCO_3$

5.2.1 Description of the experiments

Ideally, after calcium has selectively been dissolved from the steelmaking slag, calcium carbonate should precipitate from the used solvent with the help of CO_2, but without the need to add other chemicals. Otherwise, the solvent cannot be recovered and reused, at least not without expensive separation methods. The possibility of precipitating calcium carbonate by bubbling CO_2 through a solution generated by dissolving steel converter slag in an aqueous solution of ammonium salt (NH_4NO_3, NH_4Cl, or CH_3COONH_4) was tested (Paper IV). The solutions were prepared by dissolving 50 g of steel converter slag (125-250 μm) in 2.5 l of 0.5 M solution of the given ammonium salt for 2 hours at room temperature (~20 °C) and at atmospheric pressure. The residual slag was removed from the solution by sedimentation and filtration. Solution samples were taken from the solutions for Ca analysis, which was performed by ICP-AES.

A 1000-ml batch of filtered solution was stirred in a glass reactor by a magnetic stirrer. The reactor was heated using a temperature-controlled water bath. The pH and temperature of the solution were measured online. Nitrogen gas was bubbled through the solution during the heat-up. After the solution temperature had stabilized at the desired solution temperature (30 or 70 °C), the gas flow was switched to carbon dioxide. After 70 minutes of continuous exposure to the carbon dioxide flow at atmospheric pressure, the reactor was removed from the bath and the solution was filtered. The precipitate was washed and dried at 115-120 ºC overnight. The precipitates were analyzed using XRD, XRF, TC, and SEM.

5.2.2 Quality of the precipitates

The pH of the solution started to decrease immediately after the CO_2 was introduced (Figure 29), while the solution temperature increased slightly (Figure 30), the latter indicating the occurrence of an exothermic reaction. The XRD analysis showed that all the precipitates consisted of calcium carbonate as calcite (Paper IV). The XRF and TC analysis confirmed that the major elements of the precipitates were Ca and C. The sum of the other components identified by XRF amounted to only 0.14-0.21 wt-%, indicating that the purity of the calcite produced was high (close to 100 wt-%). The SEM pictures of the precipitate showed that the precipitates were in the form of rhombohedral calcite with a diameter of about 5-30 µm (Figure 31). The total conversion of calcium from the solutions to the precipitates was ~50-70%, the NH_4Cl-based solution giving the highest conversion and the NH_4NO_3-based solution giving the lowest. The solution temperature did not seem to have any significant effect on the conversion efficiency. However, the pH of the solution seems to stabilize faster at a higher temperature, which indicates a faster carbonation reaction at elevated temperatures.

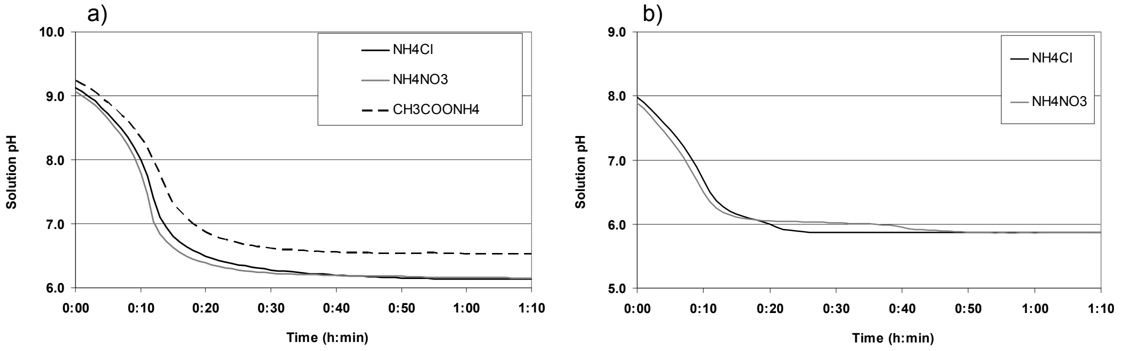

Figure 29. pH recordings of precipitation experiments at a) 30 °C and at b) 70 °C (CO_2 introduced at 0:00).

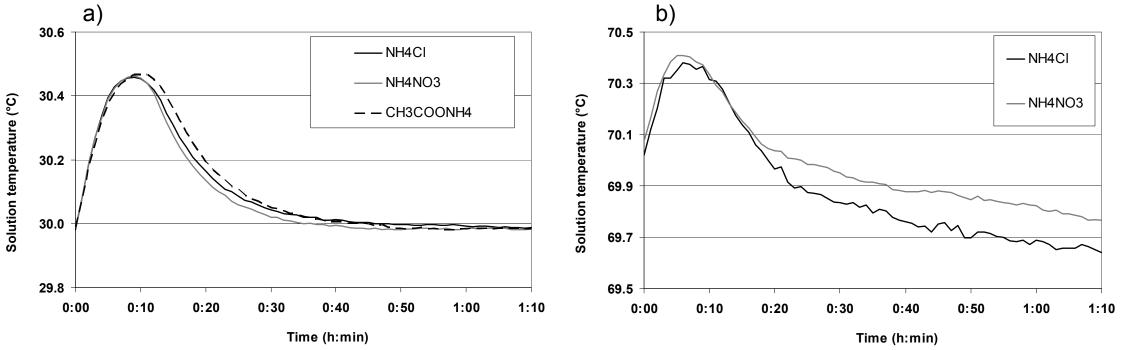

Figure 30. Temperature recordings of precipitation experiments at a) 30 °C and at b) 70 °C (CO_2 introduced at 0:00).

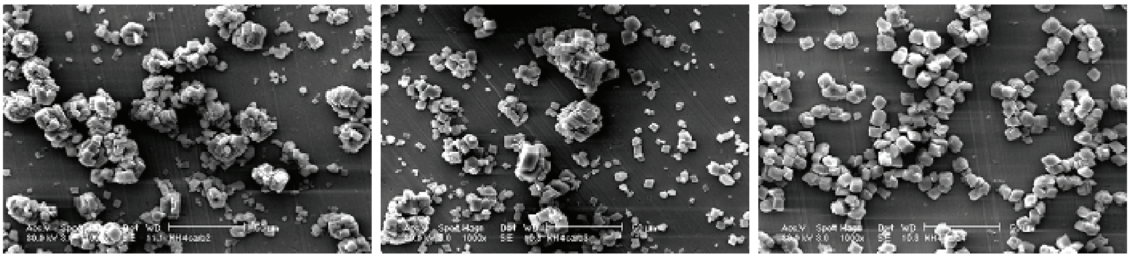

Figure 31. SEM pictures of the precipitates produced from the aqueous solution of ammonium salt and dissolved steel converter slag (Paper IV).

5.3 Feasibility analysis

The feasibility of the ammonium salt-based steelmaking slag carbonation was analyzed by calculating the costs of the method's chemical consumption and its potential for the reduction of CO_2 emissions (Paper V). As slag grinding is expected to be quite an energy-intensive process, the effect of the grain size of the slag was experimentally investigated in order to find out how large a particle size can be used. Additionally, the effect of the solid-to-liquid ratio on the dissolution of calcium from the slag was studied, because the higher the solid-to-liquid ratio, the less solvent and the smaller the reactor size that can be used.

5.3.1 The effect of the grain size of the slag

The effect of the grain size was tested by dissolving 10 g of steel converter slag (0-125, 125-250, 250-500, 500-1000, 1000-2000, and 2000-3000 μm) in a 500-ml solution of ammonium nitrate (2 M) at 30 °C and by analyzing the Ca concentration of the solution samples taken. The equipment and procedure used were very similar to those described in Chapter 4.1.1. More detailed descriptions of the experiments are presented in Paper V.

As expected, calcium dissolved most efficiently (~60% in 1 hour) and quickly from the slag fraction that had the smallest grain size (0-125 μm) (Figure 32). Most of the calcium that dissolved had already dissolved from the slag five minutes after the slag was added to the ammonium nitrate solution. Likewise, calcium dissolved quite well from the slag samples that had the second and third smallest grain sizes (125-250 and 250-500 μm) (~55% in 1 hour). On the other hand, the dissolution of the calcium was somewhat slower as it took about 30 to 40 minutes before most of the dissolving calcium had dissolved. When the grain size of the slag was above 500 μm, the extraction of the calcium was significantly lower. These results are in very good agreement with those of Kodama et al. (2008), which were based on experiments conducted with steel converter slag and an aqueous solution of ammonium chloride. In conclusion, the smaller the grain size of the steel converter slag, the higher the amount and rate of calcium extracted. Additionally, in order to avoid poor calcium extraction the steel converter slag particles should not be larger than 500 μm. Although the experimental conditions were similar to those presented in Chapter 5.1, the highest calcium extraction efficiency achieved was almost 20 %-units lower. Since the experiments presented in Chapter 5.1 were made with only 1 g of slag per experiment and slag is not a homogenous material, it might be that in the batch used in those experiments, a larger share of the calcium was in the form of free calcium oxide and dissolved more easily.

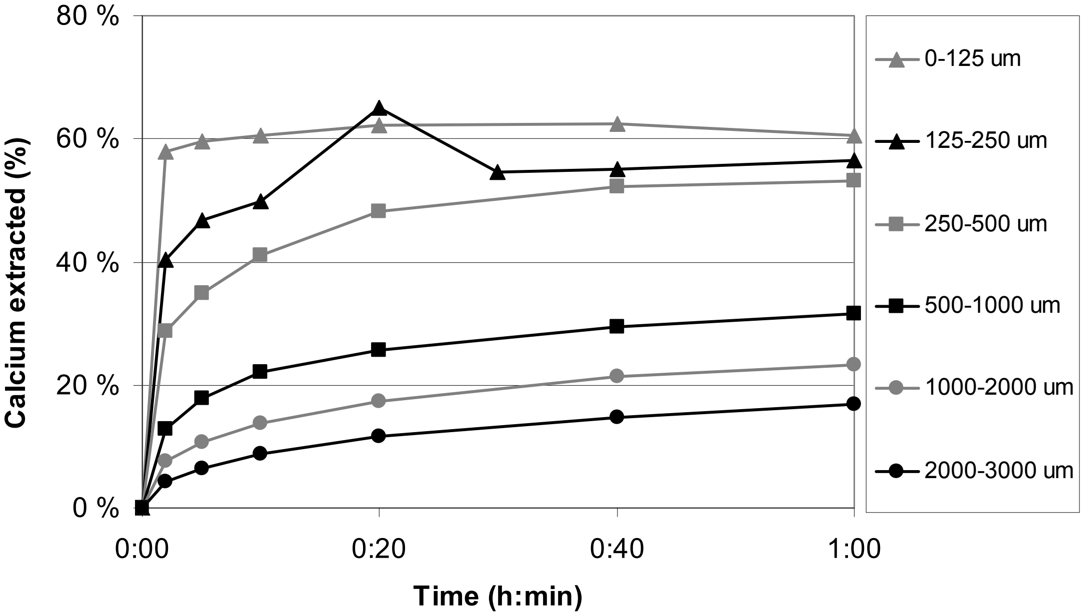

Figure 32. The effect of grain size on dissolution of calcium from steel converter slag in aqueous solution of ammonium nitrate (Paper V).

The solution temperature and pH rose (0.1-0.4 °C and ~2.5-3.8 pH units, respectively) immediately after the slag had been added to the solution (Figure 33 and Figure 34). The temperature curve indicates clearly that an exothermic reaction occurred shortly after the slag was added. The smaller the particle size of the slag, the higher the pH of the solution formed and the clearer the temperature increase.

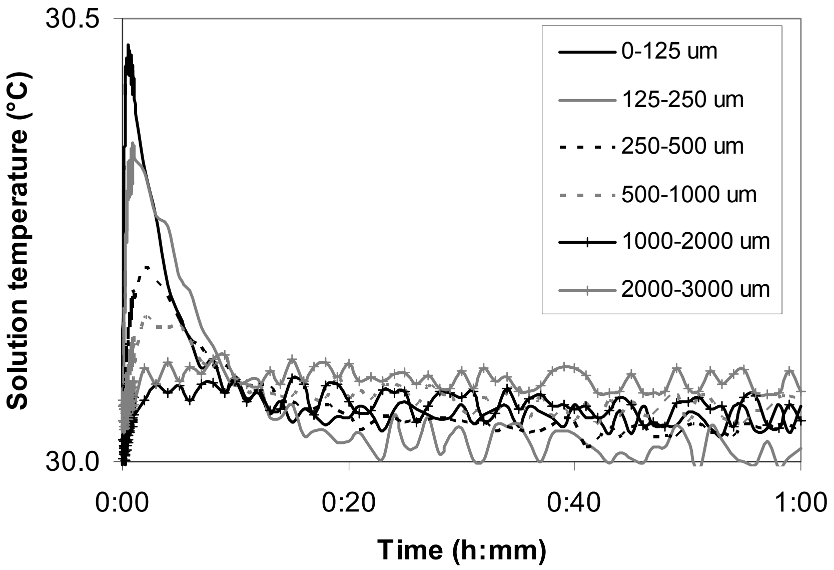

Figure 33. Solution temperature recordings of the experiments where the effect of the grain size of steel converter slag on the dissolution of calcium was tested (Paper V).

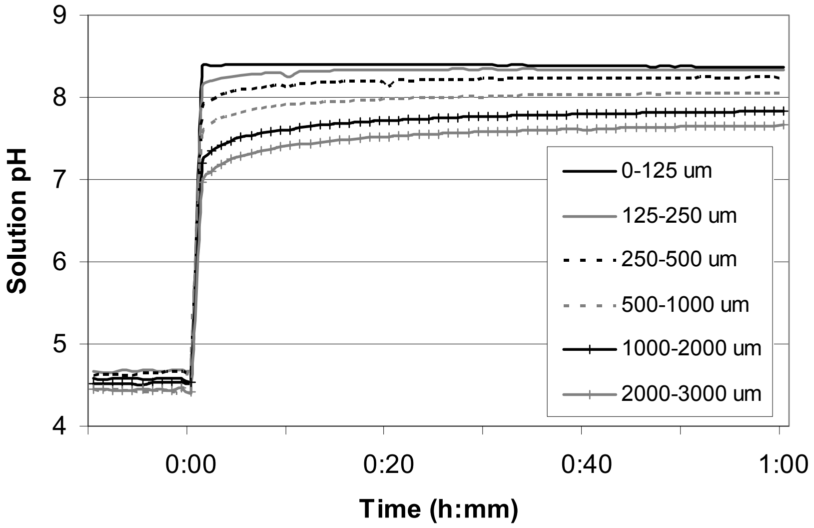

Figure 34. Solution pH recordings of the experiments where the effect of the grain size of the steel converter slag on the dissolution of calcium was tested (steel converter slag added at 0:00).

5.3.2 Solid-to-liquid ratio

The dissolution of calcium from the steel converter slag in different solid-to-liquid ratios was tested by adding a sample (1, 2, 3, 5, 10, 15, 20, and 30 g) of the steel converter slag (125-250 µm) to 50 ml of 2 M ammonium salt solution (NH_4NO_3, NH_4Cl or CH_3COONH_4) at room temperature and by analyzing the Ca concentration of the solution 1 hour after the addition of the slag (Paper V).

The best calcium extraction efficiency (~55%) was reached with the lowest solid-to-liquid ratio (20 g slag/l of solvent) (Figure 35). The dissolution of the calcium was somewhat better in an aqueous solution of ammonium nitrate than in ammonium acetate or ammonium chloride, but the difference was quite insignificant. The extraction efficiency decreased quite sharply (7-10%-units) as the solid-to-liquid ratio increased until the ratio was 60 g/l, after which the decrease was slightly milder but steady. With the highest solid-to-liquid ratio (600 g/l), only 15-18% of the calcium in the slag was dissolved. Consequently, low solid-to-liquid ratios (~ 20 g/l) in the extraction reactor should be favored and those over 100 g/l should be avoided.

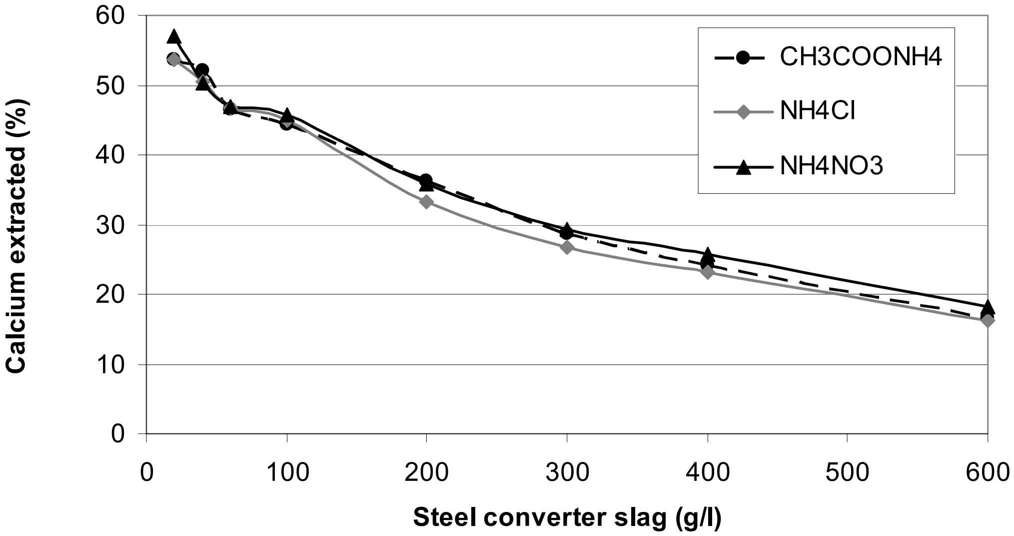

Figure 35. The effect of the solid-to-liquid ratio of the steel converter slag and solvent used on the dissolution of calcium (Paper V).

As the solid-to-liquid ratio increased from 20 g/l to 100 g/l, the calcium concentration in the solution increased about fourfold. However, when the solid-to-liquid ratio increased from that to 400 g/l, the calcium concentration only doubled, after which the concentration increased only slightly. The calcium concentration seems to start stabilizing at around 40 g calcium per l of solution, which corresponds to 1 mol of calcium per 2 moles of ammonium.

5.3.3 Economic evaluation and CO_2 balance

According to the solid-to-liquid ratio experiments, a 2 M aqueous solution of ammonium nitrate, ammonium acetate, or ammonium chloride is able to hold about 40 g calcium per liter of solution. Assuming that at least 60% of the calcium in the steel converter slag can be dissolved, if the slag is recycled sufficiently many times and that the Ca content of the slag is 32 wt-%, then 19 g calcium is dissolved per 100 g slag (Paper V). If 1 liter of 2 M solution is used, then 208 g slag is needed to form a solution containing 40 g calcium per liter of solution. This amount should bind 44 g CO_2 and produce 100 g $CaCO_3$. Consequently, in order to bind 1 t of carbon dioxide, 4.7 t of steel converter slag is consumed, and 2.3 t of $CaCO_3$, as well as 3.4 t of residual slag, is produced (Figure 36). Although the solvent can be recycled, some make-up is needed (Said et al., 2009). Assuming that 5 wt-%[5] of the ammonium would be lost despite the recycling, 39 kg of NH_3, 122 kg of NH_4Cl, 182 kg of NH_4NO_3, or 175 kg of CH_3COONH_4 is consumed per ton of CO_2 sequestered in the carbonation step.

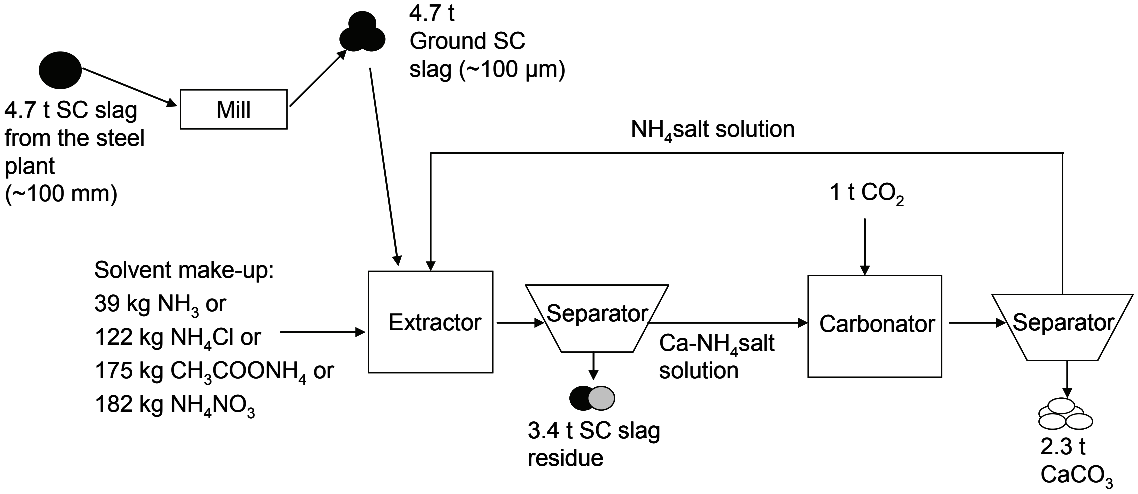

Figure 36. A simplified process scheme for sequestering 1 t of CO_2 by producing pure calcium carbonate from steel converter (SC) slag using aqueous solution of ammonium salt as a solvent.

On the evidence of the experiments where the effect of the grain size of the slag was tested, the extraction rate was very fast (~5 min) with the smallest grain size (0-125 µm) and took about 40 minutes with 250-500-µm slag. With a solid-to-liquid ratio ten times greater than in these experiments, extraction could then be roughly assumed to take about 50 minutes for 100-µm slag and about 400 minutes with 500-µm slag. At room temperature (20 °C) approximately 1 W of power is required to mix 200 g of slag in 1 liter of solution, depending on the particle size of the slag (Salminen, 2009). The power requirement of the extraction step varies depending on the particle size, solution viscosity, solution density, impeller, and reactor dimensions, for example (Harnby et al., 1985). The power requirement of the extraction step can be estimated to be roughly within 5 to 200 kWh for 4.7 t of slag, depending on the particle size.

The power required to grind the slag can be calculated using Bond's equation (Equation 32):

$$W = W_i\left(\frac{10}{\sqrt{W_{P80}}} - \frac{10}{\sqrt{W_{F80}}}\right) \qquad (32)$$

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[5] Preliminary results from the ongoing research indicate that loss of ammonium as NH_3 vapor is clearly smaller (<1 wt-%).

where W_{F80} and W_{P80} are the 80% passing size of the feed and product[6], respectively, and W_i is the work index of the slag. By using the same work index for the slag as that in Kodama et al. (2008) (30.4 kWh/t), the power consumption for grinding 4.7 t of slag is 140 kWh when the slag is ground to 100 μm and 60 kWh when it is ground to only 500 μm.

The solution pH of the precipitation experiments described in Chapter 5.2 stabilized within about 50 minutes (at 30 °C). Assuming that the power requirement for mixing the calcium carbonate-containing ammonium salt solution in the carbonation reactor was similar to that of mixing the slag and the solvent, it can be roughly calculated that stirring 2.3 t of $CaCO_3$ in the carbonation reactor would require ~5 kWh of power.

CO_2 emissions from electricity generation in Finland are about 200 g/kWh on average (Energiateollisuus Ry, 2008). Thus the power required for grinding the slag, stirring the slag and solvent in the extraction reactor (at 20 °C), and stirring the calcium carbonate particles and the used solvent in the carbonation reactor (at 20 °C) in order to bind 1 ton of carbon dioxide would generate 30 or 50 kg of CO_2 depending on the size of the slag particles (100 or 500 μm, respectively). This method would therefore clearly have negative CO_2 emissions. In addition, if the produced $CaCO_3$ precipitate was used to replace conventionally manufactured PCC, then extra CO_2 emission reductions would be gained (0.22 t/t $CaCO_3$ replaced).

By using price data collected for the ammonium salts in Mattila (2009) and assuming that the price for a larger purchase of ammonium acetate is in line with the prices of smaller purchases, then it can be roughly calculated that the use of NH_4Cl would cost €26/t CO_2, the use of NH_4NO_3 and the use of CH_3COONH_4 €40/t CO_2 (based on 5 wt-% ammonium losses/cycle). On the other hand, €227/t CO_2 could be earned by selling the produced calcium carbonate as PCC (Nordkalk Oy, 2004). The CO_2 emission allowance cost is ~ €13/t CO_2 in the European CO_2 emission trading system (Point Carbon, 2009), and thus if allowances could be sold correspondingly to the sequestered CO_2 then an additional €13/t CO_2 would be gained. Accordingly, the method has clear economic potential.

5.4 Quality of the residual slag

5.4.1 Description of the experiments

The viability of the carbonation method based on steelmaking slags and ammonium salt solutions is partly dependent on the quality of the residual slag (Figure 36). It is desirable to produce a residue that is not environmentally harmful. Therefore the effects of the aqueous solutions of the ammonium salts on the characteristics of the slag, and in

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[6] For simplification, the grain size of the feed (100 mm) and maximum grain size of the product (100 or 500 μm) were used instead of the 80 % passing size of the feed and product in these calculations.

particular on the leaching behavior of harmful elements, were investigated experimentally (Paper VI).

Batches of 100 g of steel converter slag (≤500 µm) were dissolved in 1 l aqueous solutions of ammonium acetate (CH_3COONH_4), ammonium nitrate (NH_4NO_3), or ammonium chloride (NH_4Cl) (2 M). The solutions were stirred at 500 rpm at room temperature and under atmospheric pressure. After two hours, the residual slags were removed from the solutions by filtration and washed. The residual slags were then dried at 120 °C overnight. This was repeated 4-5 times until there was enough material for the leaching tests (SFS-EN 12457-3), as well as for XRD and XRF analyses. The steel converter slag fraction used was also analyzed by XRD and XRF.

5.4.2 Results

According to the XRD analysis (Table 13), the steel converter slag was composed of calcium hydroxide ($Ca(OH)_2$), wuestite (FeO), calcium oxide (CaO), larnite (Ca_2SiO_4), srebrodolskite ($Ca_2Fe_2O_5$), and iron (Fe) (Paper VI). After extraction with the solvents the residual slags that were formed contained the same phases as the steel converter slag, except those of CaO and $Ca(OH)_2$, indicating that these had completely dissolved.

Table 13. Phases in steel converter slag and in the residual slags identified by XRD analysis (Paper VI).

Material	Phases identified
Steel converter slag	calcium hydroxide (($Ca(OH)_2$), wuestite (FeO), calcium oxide (CaO), larnite (Ca_2SiO_4), srebrodolskite ($Ca_2Fe_2O_5$), iron (Fe)
Residual slag from CH_3COONH_4 solution	larnite (Ca_2SiO_4), wuestite (FeO), iron (Fe), srebrodolskite ($Ca_2Fe_2O_5$)
Residual slag from NH_4NO_3 solution	larnite (Ca_2SiO_4), srebrodolskite ($Ca_2Fe_2O_5$), wuestite (FeO), iron (Fe)
Residual slag from NH_4Cl solution	wuestite (FeO), srebrodolskite ($Ca_2Fe_2O_5$), iron (Fe), larnite (Ca_2SiO_4)

The calcium contents of the residual slags were significantly smaller than that of the original steel converter slag, while the contents of the other major elements of the slag (Fe, Si, Mn, Mg, and V) had increased. This was expected, as these solvents had proven to be quite selective for calcium (Chapter 5.1), while, at the same time, the mass of the slag had decreased by ~25% in all the solvents. According to the results from the XRF analyses, approximately 40% of the calcium in the slag had dissolved.

The results of the leaching tests are listed in Table 14, together with the solubility data of the steel converter slag. The solubility of most of the elements from the residuals is less or similar than from the steel converter slag. On the other hand, the solubility of chromium (Cr) and V from the residual slags is significantly higher than from the steel converter slag. Furthermore, the solubility of molybdenum (Mo), chlorine (Cl), and sulphate (SO_4) from the residual slag of the experiments with the NH_4Cl solution is higher than from the steel converter slag. The solubility of nitrate (NO_3) from the residual slag of the experiments with the NH_4NO_3 solution is much higher than its solubility from the residual slags of the experiments with NH_4Cl or CH_3COONH_4, indicating that some of the anions of the NH_4NO_3 solvent (NO_3^-) combine with the slag during the extraction step. The leaching of vanadium has also been found to increase as a result of the direct aqueous carbonation of steel slag (Linz Donawitz steel slag) (Huijgen et al., 2006b), which indicates that carbonic acid also increases the solubility of vanadium and thus the leaching of vanadium cannot be prevented by carbonation.

Table 14. Solubility of the residual slags based on the shaking test (SFS-EN 12457-3) and the solubility of steel converter slag (Ruukki, 2009) (mg/kg) (Paper VI).

Element	Steel converter slag	Residual slag from CH_3COONH_4 solution	Residual slag from NH_4NO_3 solution	Residual slag from NH_4Cl solution
As	0.1-0.2	<0.006	<0.006	<0.006
Ba	2-7	0.03	0.01	0.02
Cd	0.01-0.02	<0.003	<0.003	<0.003
Cr	0.06-0.1	0.81	1.1	0.93
Cu	0.01-0.2	<0.01	<0.01	<0.01
Hg	0.001-0.003	0.001	<0.001	0.001
Mo	0.05-0.08	0.06	0.07	0.10
Ni	0.05	0.01	<0.01	<0.01
Pb	0.01-0.2	<0.01	<0.01	<0.01
Sb	0.01-0.2	<0.01	<0.01	<0.01
Se	0.05-0.1	<0.05	<0.05	<0.05
V	0.06-0.2	190	170	150
Zn	0.06-1.2	<0.01	<0.01	<0.01
Co	0.01-0.03	<0.03	<0.03	<0.03
F	1-12	<0.1	3.5	<0.1
Cl	8-20	4.6	4.9	340
SO_4	20-120	81	110	140
Br	Not available	<0.1	<0.1	<0.1
NO_2	Not available	<0.1	2.9	<0.1
NO_3	Not available	3.5	510	<0.1
PO_4	Not available	<0.1	<0.1	<0.1
Sn	Not available	<0.01	<0.01	<0.01

5.4.3 Discussion

There are no actual solubility limits that have been set so far for residual slag (Paper VI). However, there are solubility limits for different waste materials in landfills in Finland (Government Decision, 2006) and at this moment those are the only existing legal solubility limits that the results can be compared to. The solubility limit of Cr for permanent waste materials is only 0.5 mg/kg, and thus the leaching of Cr from the residual slag would prevent it from being suitable for a permanent waste landfill site. The leaching of Cr would, however, be below the solubility limit set for hazardous waste material, as well as those set for conventional waste material. Nevertheless, this Decision does not give solubility limits for V.

Ruukki's steel converter slag is a by-product (liming material) that falls under the Fertilizer Act (Fertilizer Act, 2006). When the suitability of the residual slag as liming material is considered, the main criteria are the properties required for the product (such as its neutralizing capacity). The absence of the free calcium oxide and lower calcium content strongly suggest that residual slag does not have a suitable neutralizing capacity, which is dependent on reactive lime, and thus it would probably make residual slag unsuitable for such a use. In addition, while the solubilities of the elements of the residual slags are all below the limits set for liming materials (Decree on Fertilizers, 2007; Government Decision, 2006), the leaching of V (which is not mentioned in the Government Decision) may be found to endanger human or animal health or safety or plant health, or the environment. Therefore, if no other utilization option for the residual slag is found, it would probably be handled as waste.

5.5 Discussion

The focus of this chapter was to find an alternative process route for the production of pure calcium carbonate from steelmaking slags with negative CO_2 emissions. The selective extraction of calcium from the steelmaking slags was experimentally investigated using various different solvents. It was found that amongst the solvents that were tested, ammonium salt solutions as well as lean concentrations of acetic acid and nitric acid dissolved calcium from the steel converter slag both efficiently and selectively. Since the regeneration of acid during the carbonation of the solution produced from the steelmaking slag and acid seems to prevent the efficient precipitation of calcium carbonate, ammonium salt solutions seem to be the most promising solvents for dissolving calcium selectively from the steel converter slag prior to carbonation.

Besides the two weak base-strong acid salts (ammonium chloride and ammonium nitrate) studied earlier by Yogo et al. (2005) and Kodama et al. (2008), ammonium acetate, which is a salt of a weak base and weak acid, also dissolved calcium efficiently and selectively. In these ammonium salt solutions, calcium also dissolved efficiently and selectively from the desulphurization slag. Amongst the ammonium salts tested, ammonium nitrate dissolved calcium from steel converter slag most efficiently, while the highest calcium extraction from desulphurization slag was achieved in ammonium acetate. However, from the two other types of slag of the integrated process route (blast furnace slag and ladle slag), the dissolution of calcium was poor in all the ammonium salt solutions that were tested. This is at least partly explained by the fact that both the steel converter slag and desulphurization slag contained free lime, while all of the calcium in the blast furnace slag and ladle slag was bound in silicates. However, thermodynamic equilibrium calculations indicate that the main calcium silicate phase of the steel converter slag, larnite, which is also found in desulphurization and ladle slags, can be dissolved in an aqueous solution of ammonium acetate. Additionally, synthesized larnite dissolves readily in water (Santos et al., 2009). Therefore it might be that an inert layer of, for example, SiO_2 is deposited on the reactive surface as calcium dissolves from its silicate, preventing some of the calcium from dissolving, as explained by Kodama et al. (2008). Alternatively, the calcium silicate phase is present as inclusions within the non-dissolving phases, preventing the contact of the phase with the solvent, as explained by Doucet (2010). On the other hand, the dissolution of larnite has not been confirmed by XRD, even from the steel converter slag.

The grain size of the steel converter slag had a clear effect on the rate and extent of calcium extraction from the slag. In order to avoid poor calcium extraction, the grain size of the steel converter slag should not be larger than 500 µm. A low solid-to-liquid ratio (~ 20 g/l) in the extraction reactor resulted in efficient dissolution of calcium. Furthermore, solid-to-liquid ratios over 100 g/l should be avoided. The tested capacity of the aqueous solutions of ammonium salts to hold calcium can be described as a molar ratio of 2:1, which corresponds well with the reaction in Equation 21.

$$Ca_2SiO_4(s) + 2H_2O(l) + 4NH_4Cl(aq) \rightarrow SiO_2(s) + 2CaCl_2(aq) + 4NH_4OH(aq) \quad (21)$$

Precipitation experiments were carried out with solutions containing ammonium salt and dissolved steel converter slag. It was found that calcium carbonate precipitated as rhombohedral calcite. The calcium conversion from the solution into the precipitate was 50-70%, while the purity of the precipitate was close to 100 wt-%. Compared to the acetic acid-based steelmaking slag carbonation, an aqueous solution of ammonium salt and dissolved steelmaking slag contains additional free cations (NH_4^+), which guarantees a suitable alkaline environment for the precipitation of the carbonate even during the regeneration of the solvent (Equations 16 and 33 (with CH_3COONH_4 as the ammonium salt)).

$$2Ca(CH_3COO)_2(aq) + 2H_2O(l) + 2CO_2(g) \rightarrow 2CaCO_3(s) + 4CH_3COOH(aq) \quad (16)$$

$$\begin{aligned} &2Ca(CH_3COO)_2(aq) + 4NH_3(aq) + 2H_2O(l) + 2CO_2(g) \\ &\qquad \rightarrow 2CaCO_3(s) + 4CH_3COONH_4(aq) \quad (33) \end{aligned}$$

The calculations show that the production of pure calcium carbonate from steel converter slag using ammonium salts as a solvent is associated with clearly negative CO_2 emissions. Therefore, it can be used for storing CO_2. In order to bind 1 t of carbon dioxide, 4.7 t of steel converter slag is consumed and 2.3 t of $CaCO_3$, as well as 3.4 t of residual slag, is produced. The financial gains from selling the produced calcium carbonate as PCC and possible CO_2 emission allowances corresponding to the sequestered CO_2 would clearly exceed the costs caused by the ammonium losses.

The dissolution of steel converter slag in an aqueous solution of ammonium salt was found to change the quality of the slag: the calcium content was reduced, the CaO and $Ca(OH)_2$ phases were completely dissolved, and, more importantly, the solubility of the V and Cr increased notably. The choice of ammonium salt (from among ammonium chloride, ammonium nitrate, and ammonium acetate) seemed to have an effect on the solubility of a few elements only. Because of these changes in the quality of the slag, the residual slag would probably not fulfill the property requirements set for steel converter slag used as a liming material. Therefore the residual slag would presumably have to be handled as waste, unless another suitable utilization option was invented for it.

6 Conclusions and recommendations

The possibility of reducing carbon dioxide emissions by utilizing steelmaking slags as raw material for CO_2 mineralization with a pure calcium carbonate end product was investigated in this thesis. The suitability of the acetic acid process route, suggested by Kakizawa et al. (2001), was tested first. Acetic acid was found to dissolve calcium from blast furnace slag, as well as from steel converter slag. Strong acetic acid solutions dissolved blast furnace slag completely and rapidly. The dissolution of steel converter slag was also rapid, but not as complete. A weak acetic acid solution dissolved only lime and calcium hydroxide from the steel converter slag, forming a clearly alkaline solution that contained mostly calcium acetate. Nonetheless, efficient calcium carbonate precipitation required the addition of NaOH to prevent the regeneration of acid during carbonation, as well as to increase the alkalinity of the solution in those cases where a stronger acetic acid solution was used for the dissolution step. The gas flow rate or carbon dioxide concentration did not have any significant effect on the precipitation yield, and thus it is likely that flue gases could be used as a source of carbon dioxide without the need for the energy-intensive separation of CO_2 from the flue gas.

Calcium carbonates produced from the steel converter slag by using the addition of NaOH had a significantly higher purity and whiter color than those produced from the blast furnace slag, and therefore it is quite clear that the selective dissolution of calcium is required for the production of high-purity calcium carbonate. The shape and size of the calcium carbonate precipitates was affected both by the solution temperature and the amount of sodium hydroxide added. The precipitate formed at low temperatures by adding sodium hydroxide had a rhombohedral particle shape, very high brightness and small particle size. The main obstacle to the acetic acid-based steelmaking slag carbonation is the use of sodium hydroxide, which prevents the efficient recycling and re-use of the chemicals. Preliminary process calculations revealed that chemical costs make the process clearly too expensive for CO_2 sequestration. Indirect CO_2 emissions from the production of the chemicals consumed in the process would most probably exceed the amount of CO_2 fixed during carbonation. Furthermore, a CO_2 sequestration method that consumes lots of chemicals can hardly be considered environmentally acceptable.

Because the production of pure calcium carbonate from steelmaking slags was not feasible with acetic acid, various other solvents were tested. Three ammonium salt solutions dissolved calcium from the steel converter slag selectively and almost as efficiently as acids. Besides the two weak base-strong acid salts (ammonium chloride and ammonium nitrate), ammonium acetate, which is a salt of a weak base and weak acid, also dissolved calcium efficiently and selectively. The grain size of the steel converter slag had a clear effect on the rate and extent of calcium extraction from the slag. In order to avoid poor calcium extraction the grain size of the steel converter slag should not be larger than 500 µm. It was found that the capacity of an aqueous solution of ammonium salt to hold calcium can be described as a molar ratio of 2:1.

Ammonium salt solutions also dissolved calcium efficiently and selectively from desulphurization slag, while the dissolution of calcium from ladle slag and blast furnace slag was poor. Consequently, the ammonium salt-based carbonation method is not suitable for all kinds of calcium-containing waste/by-product materials.

An aqueous solution of ammonium salt and dissolved steelmaking slag contains additional free cations (NH_4^+), which allows the precipitation of calcium carbonate during CO_2 bubbling. The precipitated calcium carbonates were very pure and in the form of rhombohedral calcite. It was calculated that the production of pure calcium carbonate from steel converter slag by using ammonium salts as a solvent has clearly negative CO_2 emissions. Since storage capacity depends on the amount of suitable raw materials available (such as steel converter slag and desulphurization slag), this method has potential only for minor-scale, yet significant, CO_2 storage. A clear advantage is, however, that it uses a low-value by-product as its raw material and has economic potential. An additional advantage is gained if the produced calcium carbonate precipitate is used to replace conventionally manufactured PCC. However, the method changes the quality of the slag and unless a suitable utilization option is invented for it, the residual slag would probably be handled as waste. While this will, it is hoped, not prevent slag from being used as a raw material for CO_2 mineralization, attention should be paid to the increased solubility of V and Cr.

6.1 Significance of this work

Mineral carbonation research is currently mainly at the level of laboratory-scale research and quite major improvements are still needed before it can provide a real possibility for the reduction of CO_2 emissions. While steelmaking slag-based carbonation does not have a very significant CO_2 reduction capacity, most of the findings of this thesis can also be applied to the carbonation of natural silicate minerals. Therefore this work contributes to the development of mineral carbonation as a CCS method, providing both experimental and process simulation-based data on carbonation.

This work shows that the acetic acid process route as such is not suitable for the reduction of CO_2 emissions, as the calcium carbonate production is too low without additional chemicals that provide increased alkalinity for the system and prevent the regeneration of the acid during the calcium carbonate precipitation. However, the acetic acid process route can be used for producing very pure calcium carbonate from steel converter slag. This is expensive because the addition of the base that is required prevents the efficient recycling and re-use of the chemicals.

The dissolution behavior of various different steelmaking slags has not been investigated before as extensively as it is here; the effects of different solvents, temperature, the grain size of the slag, and time have been studied in this work. It has been shown that besides the two weak base-strong acid salts (ammonium chloride and ammonium nitrate), ammonium acetate, which is a salt of a weak base and weak acid, also dissolved calcium efficiently and selectively from steel converter slag and desulphurization slag.

This thesis shows that very pure calcium carbonate can be produced from steel converter slag using aqueous solutions of ammonium salts as a recyclable solvent, with clearly negative CO_2 emissions and economic potential. Nonetheless, the method is not suitable for just any calcium-containing waste/by-product materials, but should be applicable for at least those that contain free calcium oxide. Having an alkaline solution prior to carbonation does not in itself guarantee efficient carbonate precipitation, but an aqueous solution of ammonium salt and dissolved steelmaking slag has an additional free cation, which creates a suitable environment for carbonate precipitation.

Previous to this work, the effects of aqueous ammonium salt-based carbonation on the characteristics of the steelmaking slag (i.e., the quality of the residual slag) had not been studied in detail. It was found that the solubility of both vanadium and chromium increased notably, indicating that more attention has to be paid to the effects of the method on the quality of the raw material.

6.2 Recommendations for future work

The production of pure calcium carbonate from steel converter slag, and probably also from desulphurization slag, with reduced CO_2 emissions is possible with aqueous solutions of ammonium salts as a recyclable solvent. Although this shows economic potential, the minimization of ammonium losses is extremely important and should be investigated in detail. Additionally, the suitability of the produced calcium carbonate precipitate for use as a commercial product has to be explored further. Attention should also be paid to the increased solubility of V and Cr from the residual slag. Furthermore, the degree of oxidation of the Cr in the residual slag should be investigated, as Cr(VI) is considered toxic, while Cr(III) is a necessary trace element for mammals (Reijonen, 2009). The necessary next step with this method is the designing and building of a larger-scale process combined with the detailed analysis of chemical kinetics and reaction mechanisms in order to find out if the process is suitable for industrial use.

For climate change mitigation purposes, the ammonium salt-based method does not have enough CO_2 storage capacity potential. Therefore, major efforts should also be put into natural magnesium silicate-based mineral carbonation research. This research should include at least attempts to find alternative solvents for enhancing the dissolution of the magnesium prior to or during carbonation, as well as alternative and more energy-efficient routes to produce $Mg(OH)_2$ (or another form of reactive magnesium) for stepwise gas-solid carbonation.

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