Assessment of the Potential Carbon Footprint of Engineered Processes for the Mineral Carbonation of PGM Tailings

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by

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minerals to metals
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Abstract

Mineral carbonation is a carbon sequestration technology that entails the reaction of CO_2 with oxides or silicates of magnesium, calcium or iron to produce stable carbonate compounds. Magnesium-rich tailings from the platinum industry in South Africa have been identified as a potentially viable and attractive feedstock for CO_2 sequestration through mineral carbonation. Many of the strategies proposed to enhance the dissolution kinetics of silicate minerals, such as the use of elevated temperatures and pressures and chemical additives, as well as pre-treatment through mechanical and thermal activation, are energy intensive and will thus reduce the net CO_2 sequestration capacity of the overall mineral carbonation process. As a result, there is growing recognition of the need to evaluate the processes using life-cycle based approaches and tools to ensure they result in net CO_2 reduction. However, to date, research and development has focused primarily on the optimisation of extraction and/or carbonation efficiencies, with specific emphasis on the relatively reactive silicate minerals, such as olivine and serpentine.

This project seeks to investigate the viability of using pyroxene-rich PGM tailings for the sequestration of CO_2, with specific emphasis on net carbon neutrality. Promising mineral carbonation processes have been identified on the basis of an extensive literature review, and include the: ammonium salts pH swing, Lackner's HCl multi-stage, gas-solid Åbo Akademi University process, direct aqueous process, and mineral acid pH swing. Material and energy balances were then conducted for these processes on the basis of the sequestration of 1 ton of carbon dioxide, using Aspen Plus v8 simulation software package. The material and energy data were then used to determine the total carbon footprint contributions, through the use of SimaPro v 7.7.3. life cycle assessment software.

The selected carbonation processes were found to release more carbon dioxide than the process sequesters. The carbonation process resulting in the most emissions released was found to be Lackner's multi-stage process (18 295 kg-CO_2e), followed by the ammonium salts process (8 798 kg-CO_2e), per ton carbon dioxide sequestered. The carbonation process resulting in the least emissions released was the solid Åbo Akademi University process (1 354 kg-CO_2e), followed by the gas-solid direct aqueous process (2 364 kg-CO_2e), as well as the mineral acid pH swing process (3 126 kg-CO_2e). The most carbon emissions intensive contributions to the carbon footprint were found to be heat requirements and chemical reagent make-up, which generally accounted for more than 85% of total emissions when combined.

Aqueous processes generally incurred a much higher carbon footprint, despite using relatively lower temperatures than the gas-solid ÅAU process. This was attributed to the higher quantities of water used in the aqueous processes that, in some cases, were subject to phase change via, for example, evaporation. Additionally, the production of make-up chemical reagent, alone, was found to result in emissions that exceeded the carbon dioxide sequestered for four of the five selected processes (ammonium salts process, Lackner's HCl multi-stage, direct aqueous, mineral acid pH swing). The potential to reduce emissions associated with heat generation could be achieved through the exploration of heat integration and cleaner alternative sources of heat, for the potentially feasible processes. On the other hand, the carbon dioxide emissions associated with make-up reagent could be reduced through the use of cleaner input materials as well as by increasing the recycle ratios to reduce external reagent requirement.

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To my late parents, Sam and Constance, and my dearest sister Ruth, this is for you.

May your souls rest in everlasting peace.

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Glossary

ÅAU	Åbo Akademi University
AS	Ammonium sulphate, $(NH_4)_2SO_4$
Aspen Plus	Market leading chemical process simulation and optimization software
atm	Unit of pressure, equivalent to 101 325 Pa, 1.01325 bar
Background	Processes on which no or, at best, indirect influence may be made by the decision maker for which a life cycle assessment study is carried out
BP	Petroleum company, *formerly known as British Petroleum*
BRPM	Bafokeng Rasimone Platinum MineJoint, South African based platinum mining company
Ca	Calcium, Ca^{2+} as calcium ions, CaO as calcium oxide
$CaSiO_3$	Calcium silicate, wollastonite
CCS	Carbon capture and storage
CFC	Chlorofluorocarbon
CH_4	Methane, *also natural gas*
CH_3COOH	Acetic acid
CH_3COO^-	Acetate ion
Clinopyroxene	Monoclinic pyroxenes, either sodic or calcic, $(Na,Al,Ca,Mg,Fe)_2SiO_6$
CO_2	Carbon dioxide
CO	Carbon monoxide
CO_2 Sequestration	Long-term storage of carbon dioxide
Cradle-to-grave	Life cycle assessment from resource extraction to disposal
Cradle-to-gate	A partial product life cycle assessment, from resource extraction to through the production of the studied product, excluding use or end-of-life stages.
Direct	*In reference to carbonation process routes*, occurring in a single process step
EDTA	ethylenediaminetetraacetic acid
EIA	Energy Information Administration
EIO-LCA	Economic input-output life cycle assessment
ELECNRTL	Electrolyte non-random two-liquid property method
EOR	Enhanced oil recovery

EPA	Environmental Protection Agency
Ex-situ	Out of natural place, i.e., above ground
Fe	Ferric iron, Fe^{2+} as iron ions, FeO as iron oxide
$FeSiO_3$	Iron (II) silicate, Ferrosilite
Fe(III)	Ferrous iron, Fe^{3+} as iron ions
Foreground	Processes which are under control by the decision maker for which a life cycle assessment study is conducted
Gate-to-gate	A partial life cycle assessment focusing on only one value-added process in the entire production chain
GTL	Gas to liquids
GW·h	Gigawatt hour
GWP, GWP100	Global warming potential, GWP over a 100-yr time horizon
H+	Hydrogen ion, proton
HCO_3^-	Bicarbonate ion
HCOOH	Formic acid
H_2CO_3	Carbonic acid
HFC	Hydrofluorocarbon
HNO_3	Nitric acid
H_3PO_4	Phosphoric acid
H_2SO_4	Sulphuric acid
Heat integration	A process engineering technique used to minimise overall process energy consumption
Heat-treatment	Heating of a mineral to remove chemically bound water, e.g., serpentine, *also HT*
IEA	International Energy Agency
Impala	South African based platinum mining company
Indirect	*In reference to carbonation process routes*, reactive components (Ca/Mg) are first extracted from the mineral matrix prior to carbonation in a separate step
In-situ	In deposit
IPCC	Intergovernmental Panel on Climate Change
IPCC-AR5	Intergovernmental Panel on Climate Change Assessment Report 5
ISO	International Organisation for Standards
kg-CO_2e	kilograms of carbon dioxide equivalents

KOH	Potassium hydroxide
KW	Kilowatt, 10^3 W
LANL	Los Alamos National Laboratory
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
Lonmin	South African based platinum mining company
M^{2+}	Metal ion
MCT	Mineral carbonation technologies
Mg	Magnesium, Mg^{2+} as magnesium ions, MgO as magnesium oxide
$MgCl_2$	Magnesium chloride
$MgCl_2 \cdot 6H_2O$	Magnesium chloride hexahydrate
MgCl(OH)	Magnesium chloride hydroxide
$MgCO_3$	Magnesium carbonate
$MgCO_3 \cdot 6H_2O$	Hydromagnesite
$Mg(NO_3)_2$	Magnesium nitrate
$Mg(OH)_2$	Magnesium hydroxide
$MgSiO_3$	Magnesium silicate, enstatite, orthopyroxene
Mg_2SiO_4	Olivine, forsterite
$MgSO_4$	Magnesium sulphate
Micron	micrometer, 10^{-6} m, μm
MJ/hr	Megajoules per hour
$M(OH)_2$	Metal hydroxide
Mt	Megatonne, 10^9 kg
MVR	Mechanical vapour recompression
MWe	Megawatt electric
NaCl	Sodium chloride
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
$NaSiO_3$	Sodium silicate
NETL	National Energy Technology Laboratory
NGCC	Natural gas combined cycle

NH_3	Ammonia
NH_4Cl	Ammonium chloride
NH_4HCO_3	Ammonium bicarbonate
NH_4HSO_4	Ammonium bisulphate
NH_4NO_3	Ammonium nitrate
NH_4OH	Ammonium hydroxide, *also ammonia water*
Northam	South African based platinum mining company
O_3	Ozone
OH^-	Hydroxide ion
P_{CO_2}	Carbon dioxide partial pressure
PGM	Platinum group metals
Plagioclase	Al-Ca-rich silicate mineral, *such as* $NaAlSi_3O_8$, $CaAl_2Si_2O_8$
ppm	Parts per million
PTGA	Pressurized thermogravimetric analyser
PWC	PricewaterhouseCoopers company
Pyroxene	Silicate mineral with general formula $(M1)(M2)(Si,Al)_2O_6$
R_{CO_2}	*A theoretical measure*, defined as the mass of ore required to convert a unit mass of carbon dioxide into carbonate.
RK-SOAVE	Redlich-Kwong-Soave equation of state model
SACCS	South African Centre for Carbon Capture & Storage
SASOL	South African based international integrated chemicals and energy company
Serpentine	Mg-sich silicate mineral, *chemical formula* $Mg_3Si_2O_5(OH)_4$
SimaPro	Widely used life cycle assessment software
Si-O tetrahedral	SiO_4^{4-} molecule
SiO_2	Silicon dioxide
Stoichiometry	The ratio of elements to each other in a mineral
t-CO_2	ton of carbon dioxide
Tailings	The waste mineral material from the processing of ore
UNIQUAC	Universal quasi-chemical property method
Weathering	The breakdown of rocks and minerals through contact with the earth's atmosphere over geological time-frames
wt%	weight percentage, *also mass percentage*

Chapter 1

Introduction

The world's energy mix is heavily biased towards fossil fuels combustion to meet global demand, providing more than 80% of the world's primary energy supply (IEA, 2013). This is expected to continue well into the 21st century (Maroto-Valer et al., 2005). The combustion of fossil fuels releases CO_2 into the atmosphere. The levels of CO_2 concentration in the atmosphere have increased from a pre-industrial value of 280 ppm to over 400 ppm in 2014 (Huisingh et al., 2015). Primarily due to anthropogenic activities, the Intergovernmental Panel on Climate Change (IPCC) has linked this increase to global climate change. This has raised concerns due to the potentially devastating effects of climate change that include rising sea levels and extreme weather patterns (IPCC-AR5, 2013). This has led some to describe global climate change as "one of the greatest threats to human survival in history" (Huisingh et al., 2015).

South Africa is a fossil fuel dependent economy with more than 95% of energy consumption coming from coal, natural gas and oil (British Petroleum, 2013). This has made South Africa the leading CO_2 emitter in Africa, 14th in the world (EIA, 2014), and the only country in Africa in the top 20 of global emitters. It is estimated that 440 Mt of CO_2 is released into the atmosphere per annum (Doucet, 2011).

The Government of South Africa has ratified the United Nations Convention on Climate Change and its Kyoto Protocol making commitments to address climate change. It identifies climate change as "one of the threats to sustainable development" that threaten to undermine development according to the Millennium Development Goals (Department of Environmental Affairs, 2011). This suggests that this is a matter of strategic importance for the country and requires serious attention to effectively address. In this regard, technological solutions that reduce or taper rising CO_2 emissions need to be explored in order to prevent adverse effects on the environment, which would undermine the development objectives of South Africa.

The combustion of fossil fuels to power economies, particularly in the developing world, is unlikely to be eliminated in the near future. This is due to the vast availability of these resources, and the relatively well understood and less costly technologies to harness energy

from these fuels. In view of this, improvements in energy efficiency, development of clean alternative energy sources, as well as carbon capture and storage (CCS) technologies are required to reduce CO_2 emissions. Improvements to energy efficiency are limited (Wang, 2011), and thus would not contribute significantly to emissions reduction. With the adoption of alternative clean energy sources being very slow, the consideration of CCS technologies to provide a more immediate solution is necessary. This technology can reduce between 85-90% of the CO_2 emissions from a large point source emitter (Leung et al., 2014). An overview of the carbon capture and storage process is presented in Figure 1-1.

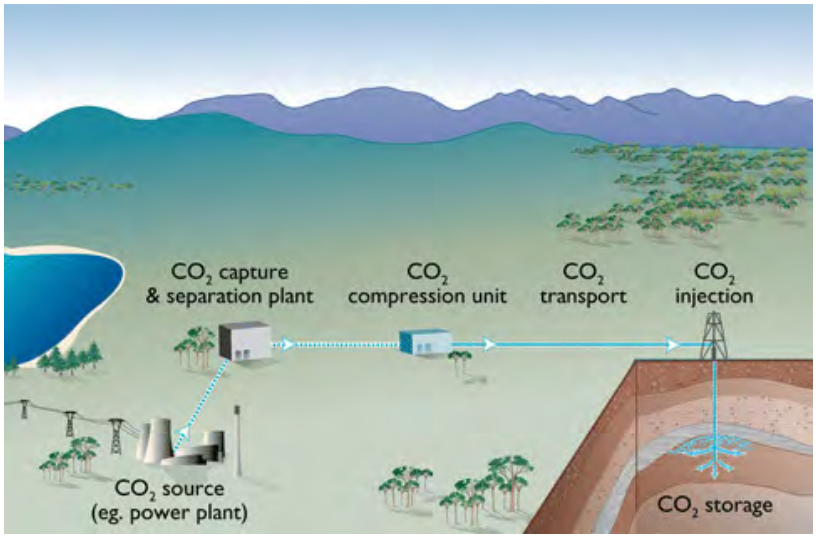


Figure 1-1: Carbon capture and storage overview schematic (CO2CRC, 2015)

The South African government has established the South African Centre for Carbon Capture & Storage (SACCS), with a view towards implementing these technologies in the country (SACCS, 2013). The IPCC (2005) states that CCS involves collection/concentration from emitters such as industrial and energy generating operations, transport to storage locations and storage away from the atmosphere for a long period of time. The storage of CO_2 can be classed into three categories: ocean storage, geological storage and mineral carbonation. Despite the general concerns with potential leakages (Park, 2005; IPCC, 2005, Teir, 2008) associated with geological and ocean storage, limited sites for geological storage exist in South Africa, and offshore basins are far from CO_2 emitters (Cloete, 2010; Viljoen et al., 2010). This suggests that implementing these technologies in South Africa may not be worthwhile, since the amounts sequestered may not be significant or the costs of sequestration too high to justify. A potential alternative to these in South Africa is mineral carbonation. It is this potential that will

be explored in this study, with a specific focus on the potential use of PGM tailings as feedstock.

1.1 Background

Mineral carbonation is a capture and storage technology that mimics the natural weathering process through the reaction of oxides or silicates of magnesium, calcium or iron with CO_2 to form stable mineral carbonates. The process is summarized by the chemical equation:

$$(Ca,Mg,Fe)SiO_{3(s)}+CO_{2(g)}\rightarrow(Ca,Mg,Fe)CO_{3(s)}+SiO_{2(s)} \quad (1)$$

The stability of the reaction products of mineral carbonation is a result of the carbon atom being at its lowest energy state in the carbonate product that provides storage on a time scale of >100,000 years (Rackley, 2010). The use of silicates in mineral carbonation is also attractive due to their abundance in nature, with a potential to sequester all CO_2 emissions from the combustion of all existing fossil fuel resources (Lackner et al., 1995; IPCC, 2005). Finally, the mineral carbonation reaction is exothermic thus presenting energy integration opportunities in a developed industrial mineral carbonation process. A schematic of the mineral carbonation process is shown in Figure 1-2.

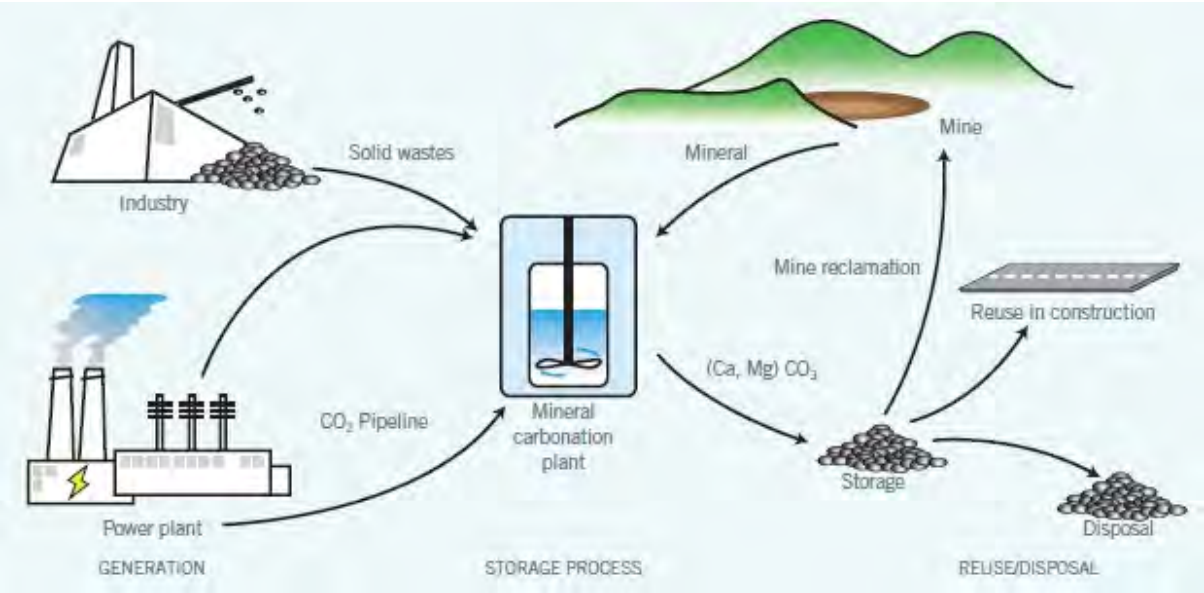


Figure 1-2: Mineral carbonation process scheme (Global CCS Institute, 2011)

1.1.1 Engineered Mineral Carbonation Processes

Since mineral carbonation mimics the natural weathering process, which occurs over geological time scales, the reaction kinetics for this process are inherently slow. Several approaches to mineral carbonation have been studied ranging from direct carbonation of solid

mineral with CO_2, to more complex multi-stage aqueous mineral carbonation routes (Rackley, 2010; Olajire, 2013). The primary focus of research in this area has been to accelerate the reaction kinetics of mineral carbonation so that it may be justified for industrial implementation. Figure 1-3 provides a summary of the mineral carbonation technologies (MCT) that have been proposed in literature. The mineral carbonation processes have been classified into ex-situ (out of natural place, i.e., above ground), in-situ (in deposit), as well as other routes that include the use of biological organisms to facilitate the carbonation process. It is evident that several process routes have been proposed within these categories. However, the subsequent discussion will focus on some of the more common ex-situ carbonation processes.

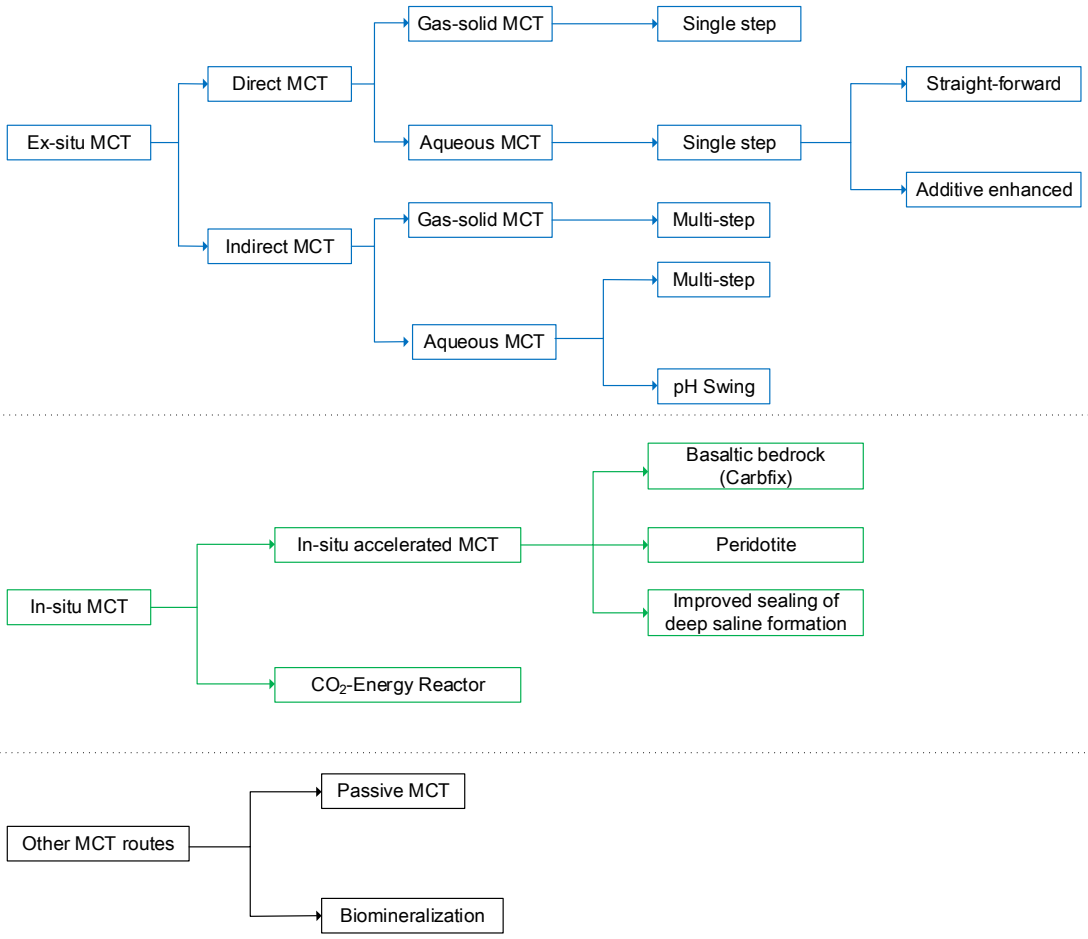


Figure 1-3: Classification of mineral carbonation process routes (adapted from Olajire, 2013)

The simplest mineral carbonation route, in terms of process design, is the direct gas/solid carbonation route. This approach is hindered by prohibitively slow reaction kinetics even at elevated temperatures and pressure (Huijgen and Comans, 2003). It has thus been virtually abandoned, though a few researchers (Fagerlund et al., 2010; Zevenhoven et al., 2011; Slotte

et al., 2013) are still conducting research in this route, albeit having developed this into a relatively more complex indirect multi-stage process.

A considerable amount of research interest has been given to the aqueous mineral carbonation routes (Huijgen and Comans, 2003). This approach makes use of water or chemical additives to accelerate the mineral carbonation process. Direct aqueous mineral carbonation, in particular, has enjoyed intense interest by a number of researchers (O'Connor et al., 2001; Gerdemann et al., 2007; Bonfils et al., 2012) who consider it to be more promising than gas-solid approaches. However, aqueous mineral carbonation involves two steps, which have conflicting optimal operating conditions: extraction of the alkaline earth metals from the silicate minerals through dissolution, followed by carbonation of the dissolved cations, through carbonate formation and precipitation. A low pH and high temperature are optimal for the dissolution step whereas the precipitation step is favoured by a high pH and more moderate temperatures (Gerdemann et al., 2007). This approach, by design, is thus limited in terms of process optimisation because of the complexity of the carbonation system (Haug, 2010).

Park et al. (2003) proposed a pH swing method, an indirect aqueous mineral carbonation approach. This approach involves dissolving silicate minerals at low pH using acid solutions and subsequently carbonating the leachate under alkaline conditions. This provides the opportunity to optimise the dissolution and carbonation reaction steps individually. It has thus been adopted by a significant number of researchers (Teir et al. 2007; Wenzhi et al., 2009; Wang and Maroto-Valer, 2011; Meyer et al., 2013; Sanna et al., 2014a). The dissolution stage is considered to be the rate-limiting step in aqueous mineral carbonation (Park and Fan., 2004; Alexander et al., 2007; Gerdemann et al., 2007; Meyer et al., 2014), and much of the research and development of engineered mineral carbonation systems has focused on methods to improve kinetics of the dissolution step.

To accelerate the dissolution kinetics, aggressive leach conditions (low pH, elevated temperatures and pressures, strong acids) and/or pretreatment such as mechanical and thermal activation have been suggested (Gerdemann et al., 2007; Teir et al., 2007; Wang and Maroto-Valer, 2011). However, these conditions are relatively energy intensive (Maroto-Valer et al., 2005; Gerdemann et al., 2007), and can significantly increase the CO_2 footprint of the mineral carbonation process as a result of the process energy requirements. It is important then that the sequestration benefits of the mineral carbonation solution, outweigh the environmental impact that it causes.

This is an important consideration, since the fundamental purpose of mineral carbonation technology should be to reduce, not increase CO_2 emissions. This means that for the mineral carbonation process to be a viable CO_2 emissions reduction technology, the process needs to result in negative net CO_2 emissions over its entire life cycle. This would include carbon capture and storage, transportation, materials preparation, carbonation, consumption and regeneration of reagents, and management of solid products and effluents.

1.1.2 PGM Tailings as potential feedstock

The precious metals industry in South Africa produces vast amounts of mine tailings that contain silicate minerals. In particular, the platinum industry produces 77.5 million tonnes per annum of PGM tailings that, in theory, can sequester 13.5 million tonnes of CO_2 per annum (Vogeli et al., 2011). These are dominated by magnesium and calcium silicates, and are mostly orthopyroxene (65 wt.%) and plagioclase (16 wt.%) with clinopyroxene and amphibole in smaller amounts (Meyer et al., 2014). They are available as finely ground material (Vogeli et al., 2011) due to ultra-fine grinding required to liberate small platinum group grains. This implies that mechanical activation of this feedstock would not be required (Doucet, 2011). This indicates that there is potential for PGM tailings to be used as a mineral feedstock in mineral carbonation. An additional potential benefit to the use of this particular feedstock, is the opportunity to recover residual PGM mineral values during cation extraction in carbonation operations. This could potentially improve the economics of the process.

South Africa has a number of CO_2 emission sites that are located within a 300 km radius of the PGM industry (Doucet, 2011). This makes it feasible to transport captured carbon dioxide to the tailings deposit for the purposes of mineral carbonation. Picot et al. (2011) established a world inventory which mapped carbon dioxide emissions sites to “Large and Superlarge Deposits” of silicate minerals, by linking these two data sources using ArcGIS technology. This global study identified the situation in South Africa as “favourable”, in terms of proximity, as a number of CO_2 emissions sites were within a 300 km radius from deposits of ultramafic rocks as indicated in Figure 1-4.

In particular, the Sasol Synfuels plants in Secunda (Mpumalanga) and Sasolburg (Free State) produce a highly pure stream of CO_2 (90-98%) that would require minimal separations and CO_2 capture operations (Cloete, 2006). This presents an attractive opportunity to develop a process that utilises this stream (largest global point-source polluter) and the mine tailings from the platinum industry, to create a uniquely South African carbon sequestration process.

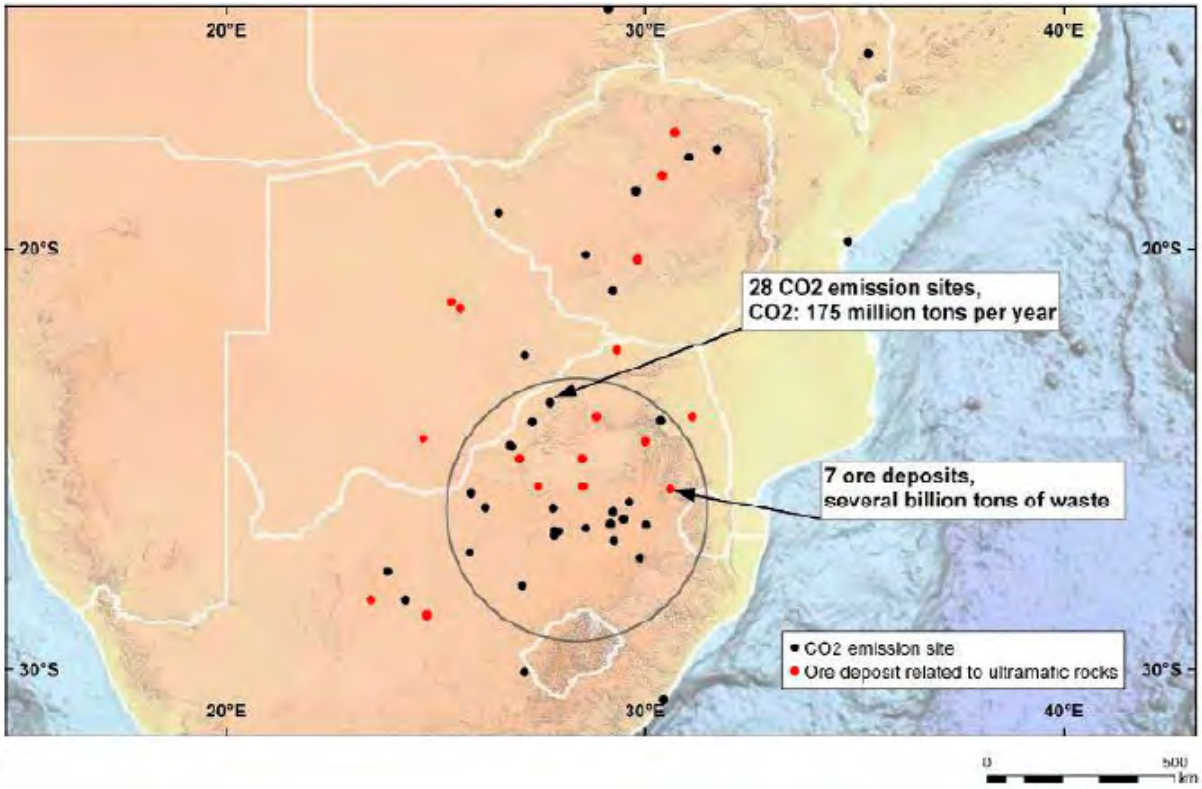


Figure 1-4: Carbon dioxide emissions sites and ultramafic rock deposits in 300 km radius (Picot et al., 2010)

However, preliminary experiments under relatively mild pH swing conditions have resulted in poor extraction efficiencies, which have been attributed to the relatively inert nature of the silicate mineral pyroxene (Meyer et al., 2014; Sanna et al., 2014a).

1.2 Problem Statement

South Africa is the continent's largest emitter of CO_2, a greenhouse gas that has been linked to climate change. Limited geological sequestration sites are available to sequester the vast amounts of CO_2 produced by industrial operations annually. Mineral carbonation is an attractive alternative that can potentially utilize the tailings produced by the platinum industry as feedstock. However, current carbonation of silicate minerals in engineered carbonation systems generally requires relatively aggressive and energy-intensive processes, and/or pretreatment to enhance the reaction kinetics. This is particularly so in the case of PGM tailings, the major component of which is pyroxene, which is very inert. This is a challenge given that a key requirement of any engineered mineral carbonation process, is that it must result in a net reduction in carbon dioxide emissions. Although a number of processes for the sequestration of carbon dioxide have been proposed, to date, rigorous and systematic studies on their carbon neutrality have been limited.

1.3 Research Objectives and Scope

The overarching aim of this study is to investigate the viability of using PGM tailings to sequester CO_2 on the basis of carbon neutrality. More specifically, this project sets out to meet the following objectives:

I. Identify potentially feasible flowsheets for the mineral carbonation of PGM tailings on the basis of literature data and information.

II. Develop mass and energy balances for the identified processes using process simulation software.

III. Establish the carbon footprint of the selected mineral carbonation processes using a life-cycle based approach.

This is a desktop study that makes use of published literature, and modelling assumptions based on literature and engineering heuristics to establish the carbon footprint of mineral carbonation processes. Experimental work was not conducted to verify or establish the technical credentials and feasibility of selected mineral carbonation processes. The identification of potentially feasible processes for the mineral carbonation of PGM tailings was based on a review of published literature and previous in-house (Vogeli et al., 2011; Vogeli, 2012; Meyer et al., 2014; Meyer, 2014) studies. The verification of the technical validity of the selected mineral carbonation processes is beyond the scope of this study. Additionally, the economic implications of the selected processes and process configurations was not evaluated.

1.4 Dissertation Layout

This dissertation consists of six chapters, including this introductory one. The introductory chapter (Chapter 1) gives an outline of the impact of carbon dioxide on the environment, and the viable storage options for carbon dioxide sequestration in South Africa, to provide a contextual background and motivation for the project. The mineral carbonation of PGM tailings is identified as potentially feasible, and a brief overview of process routes is provided. This is followed by a review of the relevant mineral carbonation related literature in Chapter 2, with specific focus on current mineral carbonation routes and engineered processes, their technical, and environmental performance. Additionally, a discussion on the selection of mineral carbonation processes to be considered is presented. As a consequence of the literature review, the methodology (Chapter 3) is developed that outlines the approach, tools and techniques used, including the definition of the goal and scope, material and energy balance evaluation, as well as inventory analysis and carbon emissions accounting. The results for selected processes are

then presented and discussed individually in Chapter 4. In Chapter 5, a detailed comparison of the performance of selected processes is undertaken and discussed alongside some general discussions on the technical feasibility of selected processes. Final conclusions are then drawn and recommendations for further studies made in Chapter 6.

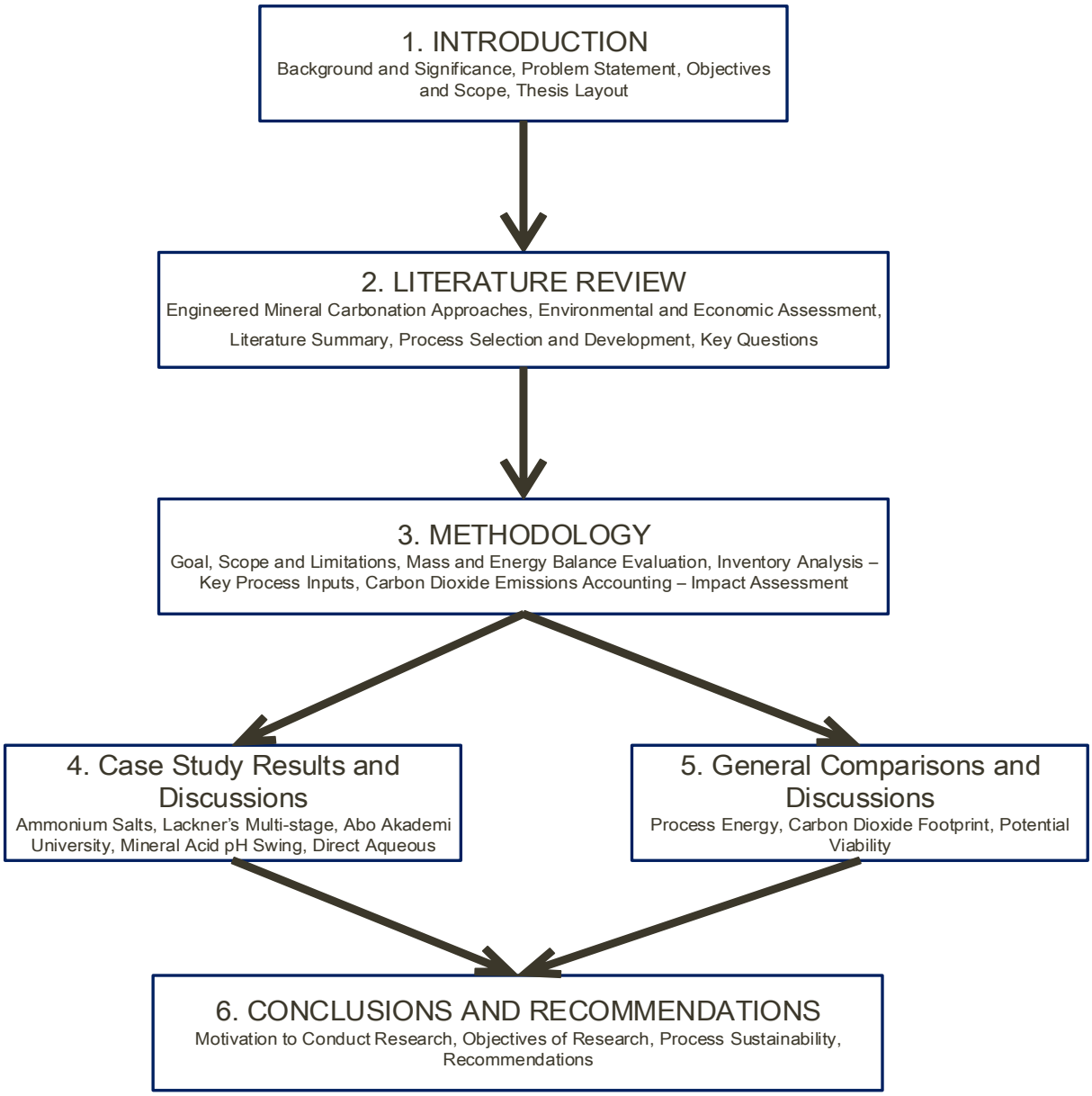


Figure 1-5: Outline of thesis layout

Chapter 2

Literature Review

This literature review begins by reviewing the existing engineered mineral carbonation processes to gain insights into the state-of-the-art of these technologies. This assists in identifying potentially feasible process options, and in determining input data for mass and energy balance modelling. An exploration of previous life cycle assessment studies of carbonation processes is conducted to identify the key issues and the techniques used in evaluating process performance from an environmental standpoint.

2.1 Engineered Mineral Carbonation Approaches

The silicate minerals suitable for carbon sequestration through mineral carbonation are listed in Table 2-1 together with their theoretical sequestration capacity, R_{CO_2}. This is a theoretical measure defined as the mass of ore required to convert a unit mass of carbon dioxide into carbonate (Gerdemann et al., 2007). The silicate minerals with the lowest R_{CO_2} values are olivine and serpentine.

Table 2-1: Direct carbonation based theoretical capacities of silicate minerals to sequester CO_2 (Meyer et al., 2014)

Mineral		Formula	Silicate Structure	Ideal Elemental Concentrations (wt%)			RCO_2[a]	Rate -log R (mol cm^{-2} s^{-1})
Group	End Member			Ca	Fe	Mg		
Feldspar								
Plagioclase	Anorthite	$CaAl_2Si_2O_8$	Framework silicate	10.3	3.1	4.8	4.4	9.3-14.5
Pyroxene								
Orthopyroxene	Enstatite	$MgSiO_3$	Inosilicate	0.3	4	20.8	2.4	13.9-14.5
Clinopyroxene	Diopside	$CaMgSi_2O_6$	Inosilicate	18.5	0.5	11.3	2.4	14-12
	Augite	$CaMgSi_2O_6$ + (Fe,Al)	Inosilicate	15.6	9.6	6.9	2.7	13.5
Pyroxenoid	Wollastonite	$CaSiO_3$	Inosilicate	31.6	0.5	0.3	2.8	12.4
Olivine								
Olivine	Forsterite	Mg_2SiO_4	Neosilicate	0.1	6.1	27.9	1.8	12
	Fayalite	Fe_2SiO_4	Neosilicate	0.6	44.3	0.3	2.8	10.8
Serpentine								
Serpentine	Antigorite	$Mg_3Si_2O_5(OH)_4$	Phyllosilicate	<0.1	2.4	24.6	2.1	-

[a] Mass ratio of ore necessary to carbonate unit mass of CO_2

Apart from their theoretical sequestration capacity, these silicates also differ in their structures and reactivity. Meyer et al. (2014) ranks the reactivity of magnesium silicates as decreasing in the order: olivine>serpentine>pyroxene. The reactivity of silicate minerals has been attributed to their structure. The structures of the ortho- and phyllo- silicates olivine and serpentine are less rigid, and held together by weaker bonds in comparison to pyroxene group minerals, that are an infinite, single chain of silica tetrahedral. This makes olivine and serpentine more reactive, as the cations are more accessible to the reagent (Meyer et al., 2014).

The natural weathering of these minerals, from which mineral carbonation is adapted, occurs over geological time scales. Consequently, the reaction kinetics of the mineral carbonation process would be very slow for industrial implementation under natural conditions. Engineered carbonation processes have thus been proposed and developed to accelerate the natural weathering process through the chemical and physical manipulation of the silicate mineral. This has included the use of high temperatures, high pressures, chemical reagents, and in some cases multiple process steps. This section will discuss the existing mineral carbonation process routes, their development, as well as the impact of changing process parameters on these routes.

2.1.1 Gas-Solid Mineral Carbonation

Direct gas-solid carbonation is considered the simplest mineral carbonation approach in terms of process design. This route also offers the best prospect of effective utilization of the heat released from the reaction (Rackley, 2010). This process was one of the first proposed for the purposes of mineral carbonation by researchers at the Los Alamos National Laboratory (LANL) (Lackner et al., 1995).

The main drawback of this process is that the carbonation reaction proceeds very slowly, and requires supercritical operating conditions (300 °C and 340 bar P_{CO_2}) to obtain reasonable reaction rates (Huijgen, 2007). A study conducted by Zevenhoven and Kohlmann (2002) found no detectable carbonation when the temperature was held constant at 200 °C in a pressurized thermogravimetric analyser (PTGA). Low conversions were reported even after samples were heated up to 1000 °C to release MgO from the silicate mineral. Secondly, increasing the temperature is thermodynamically limited since high temperatures favour gaseous CO_2 instead of the carbonate compound due to entropy effects (Huijgen, 2007). This direct approach has been largely abandoned by most researchers (Olajire, 2013).

Studies then progressed towards a two-step route converting the silicate mineral to magnesium oxide at high temperatures and pressure to accelerate carbonation (Lackner et al., 1995;

Zevenhoven et al., 2002). Zevenhoven et al. (2002) defines this process as occurring according to the reactions in equations (2) and (3):

$$xMgO.ySiO_2.zH_2O_{(s)} \rightarrow xMgO_{(s)} + ySiO_{2(s)} + zH_2O \quad (2)$$

$$MgO_{(s)} + CO_2 \rightarrow MgCO_{3(s)} \quad (3)$$

The rate of carbonation of magnesium oxide under atmospheric conditions was reported to be too slow for practical purposes, whereas that of magnesium hydroxide was identified as promising (Lackner et al., 1997). This led these researchers to develop a processing scheme based on magnesium hydroxide. Studies conducted by Teir et al. (2006) demonstrated the impact of increasing temperature and pressure on the conversion of magnesium hydroxide to magnesium carbonate. Their findings showed that increasing the temperature and pressure for the carbonation of magnesium hydroxide increased the extent of carbonation. Table 2-2 indicates that the conversion in 6 hours did not exceed 60% even with temperatures exceeding 500 °C and a pressure of 45 bar, using commercially produced magnesium hydroxide. This is a serious limitation since substantial energy is required to achieve these conditions, with a modest return in terms of conversion.

Table 2-2: Conversion of $Mg(OH)_2$ to $MgCO_3$ at various temperature/pressure conditions after 6 hrs (Teir et al., 2006)

Pressure bar	Temperature °C	Conversion %
1	370	6
12	460	19
35	495	50
35	510	46
35	525	44
35	540	43
40	510	60
40	525	37
40	540	40
45	525	44

The magnesite produced by the carbonation reaction builds up on the surface of the silicate mineral particles creating a diffusion barrier that results in the slowing of the carbonation of magnesium hydroxide (Zevenhoven and Teir, 2004). Through the use of a fluidized bed

reactor, Teir et al. (2004) demonstrated that this layer could be removed through attrition and abrasion.

Through further developments of this work, researchers at the Åbo Akademi University (ÅAU) have proposed a process that makes use of ammonium sulphate (AS) to convert the silicate mineral to magnesium hydroxide, through a high temperature and pressure solid-solid extraction reaction (Fagerlund et al., 2009). This reaction initially produces magnesium sulphate which is dissolved in water and subsequently reacted with ammonium hydroxide to precipitate, first impurities, then eventually the reactive magnesium hydroxide compound. This compound is finally reacted with gaseous carbon dioxide to produce solid and stable magnesite. A simple block-flow diagram demonstrating the main stages of the proposed process is presented in Figure 2-1.

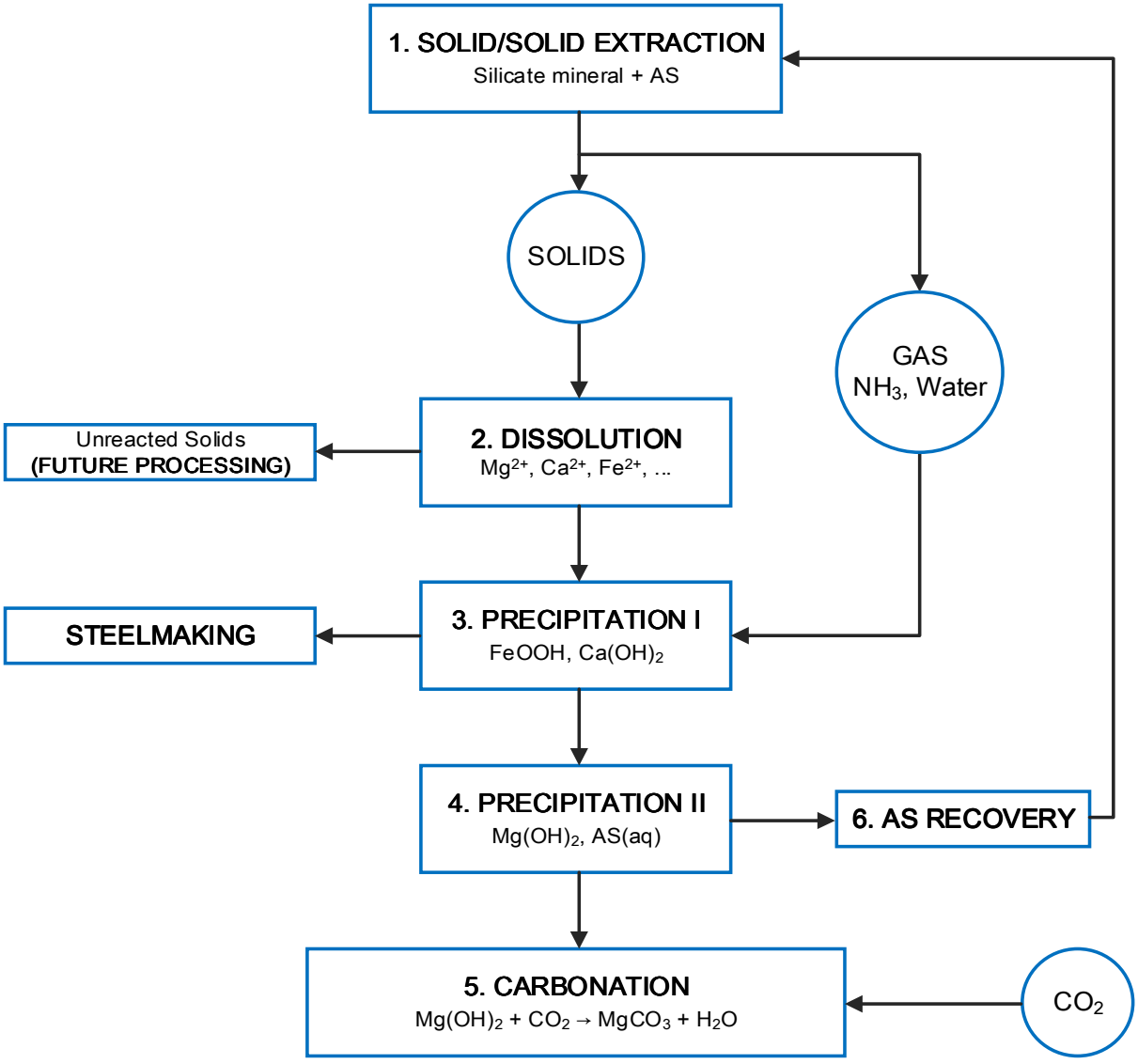


Figure 2-1: Schematic of Åbo Akademi University multi-stage process (adapted from Romao et al., 2012)

The first step in the process proposed by researchers at ÅAU is the extraction of magnesium from the silicate mineral using ammonium sulphate. Nduagu et al. (2012a) reported that the maximum extraction obtained in his work was 64%-66% at 400-440 °C using a sample of serpentine with a particle size of 75-125 microns. This produces solid magnesium sulphate, and gaseous ammonia and water. A slightly lower (53%) magnesium extraction was reported when the particle size fraction of 125-250 microns was used at about the same temperatures (Nduagu, 2012). The magnesium sulphate is then dissolved into solution and through a series of precipitation steps, is converted to magnesium hydroxide through reaction with water and ammonia, which also regenerates the ammonium sulphate reagent. This is followed by carbonation, which initial experimental data showed that the highest degree of conversion in the carbonation stage was 23%, obtained by using $Mg(OH)_2$ generated from serpentinite (Fagerlund et al., 2010). These experiments were conducted in a fluidized bed system that used high pressures (2.85 MPa) and temperatures (500 °C). A synthetic sample of $Mg(OH)_2$ was used as feedstock, in another set of experiments. The authors reported that the process only managed 50% $Mg(OH)_2$ carbonation using this feedstock (Zevenhoven et al., 2011).

2.1.2 Direct Aqueous Mineral Carbonation

This is an approach that has garnered much research interest because of its better reaction kinetics in comparison to the gas-solid route. It is considered to be relatively simple since the two reaction steps in aqueous carbonation, dissolution and carbonation occur in a single step.

This process is based on the observation that natural weathering is enhanced by the presence of water. A process was developed by O'Connor et al. (2000) based on this phenomenon. In this process, CO_2 at high pressure reacts in an aqueous suspension of the silicate mineral. The authors theorized that CO_2 is dissolved in water to produce carbonic acid, which facilitates the extraction of the reactive cation (Mg^{2+}, Ca^{2+}) from the mineral matrix. The free cation then reacts with bicarbonate ions generated by the dissociation of carbonic acid to produce a solid carbonate compound (O' Connor et al., 2000).

The process route thus involves three reaction steps that occur in a single reactor (Rackley, 2010):

Step 1: Carbon dioxide dissolves in water to form carbonic acid that dissociates to produce protons (H^+) and bicarbonate ions (HCO_3^-), resulting in mildly acidic conditions:

$$CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)} \rightarrow HCO_{3(aq)}^- + H^+_{(aq)} \quad (4)$$

Step 2: The H^+ free protons extract Ca/Mg/Fe cations from the mineral matrix, e.g. for forsterite:

$$Mg_2SiO_{4(s)} + 4H^+_{(aq)} \rightarrow 2Mg^{2+}_{(aq)} + SiO_{2(s)} + 2H_2O_{(l)} \quad (5)$$

Step 3: The metal and bicarbonate ions combine and form carbonate precipitate:

$$Mg^{2+}_{(aq)} + HCO^-_{3(aq)} \rightarrow MgCO_{3(s)} + H^+_{(aq)} \quad (6)$$

A large body of work has been done on this route that seeks to maximize the reaction rate and optimize the process (O'Connor et al., 2000; O'Connor et al., 2001, Gerdeman et al., 2002; O'Connor et al., 2005; Gerdemann et al., 2007). In developing the process, the first step would be to maximise the reaction rate by modifying the process conditions such as particle size, operating temperature, CO_2 pressure and chemical additives.

Impact of Temperature and Pressure

The increase in temperature from ambient conditions generally increases the reaction rate of the direct aqueous carbonation process. On the other hand, this reduces the solubility of carbon dioxide in solution and makes the carbonation reaction less thermodynamically favourable (Gerdemann et al., 2002). This suggests that there are limits to the extent to which the temperature can be increased without significantly affecting overall carbonation through reducing carbon dioxide solubility. This, in turn, would indicate that there are optimal conditions which can be found that balance reaction rate with thermodynamic stability of the carbonate and CO_2 solubility.

In work conducted by Gerdemann et al. (2002) at the Albany Research Center, relatively low temperatures less than 50 °C were found to favour the formation of hydromagnesite precipitates. Temperatures in the range between 100 °C and 150 °C were found to be the area of stability of magnesite, for CO_2 pressure of 1 bar as well as 150 bar as indicated in Figure 2-2. The region of magnesium carbonate stability can be increased by increasing the pressure above atmospheric (Gerdemann et al., 2002). The increase in pressure also enhances the reaction rate due to the increased concentration of dissolved CO_2. This is also because the reaction is pushed towards completion due to volume change as a result of gas consumption as the CO_2 is converted to the carbonate compound (Gerdemann et al., 2002).

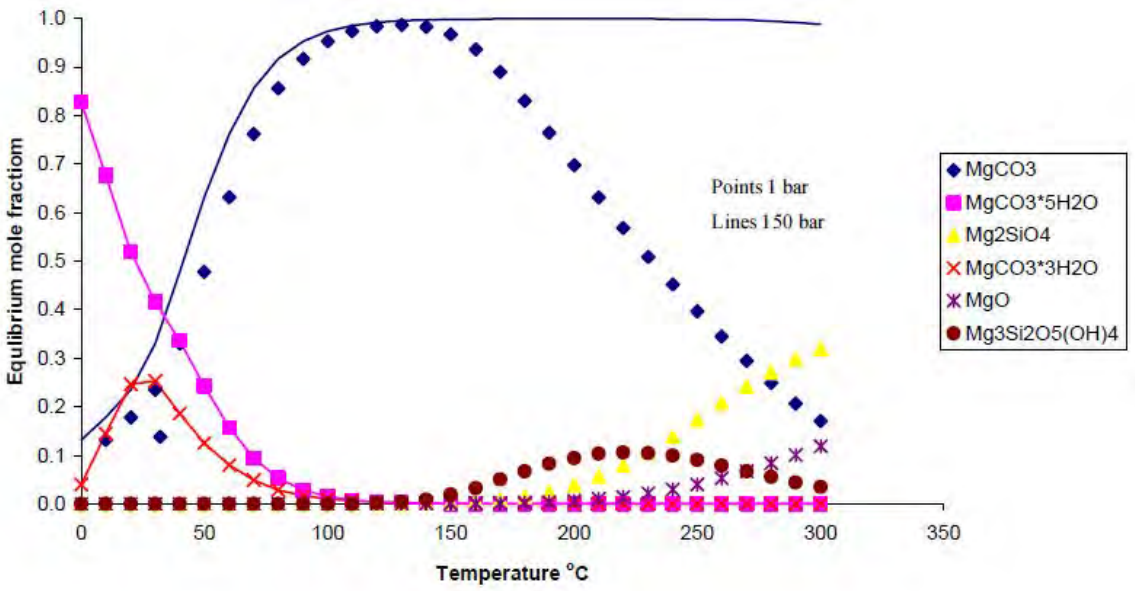


Figure 2-2: Thermodynamic equilibrium compositions for Mg_2SiO_4-CO_2-H_2O system (Gerdemann et al., 2002)

Studies on olivine conducted by the authors to establish the effect of pressure on extent of carbonation, demonstrated this increase in carbonation from atmospheric up to 250 atm (Gerdemann et al., 2002) as presented in Figure 2-3.

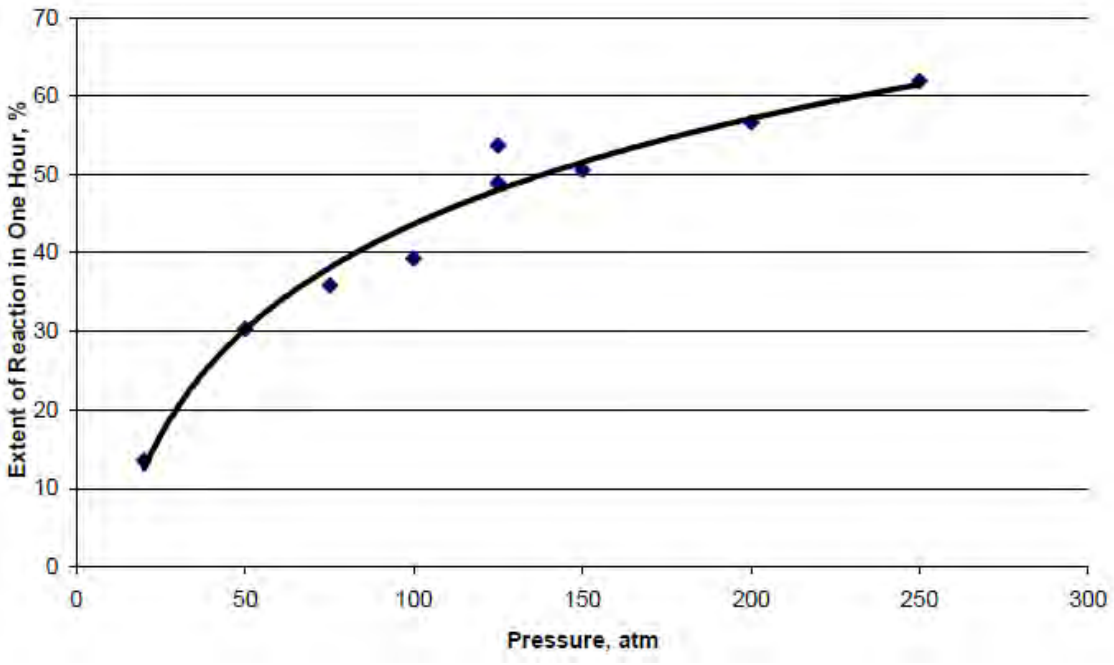


Figure 2-3: The effect of pressure on the extent of carbonation (Gerdemann et al., 2002)

Through the research from the Albany Research Center (now called the National Energy Technology Laboratory - NETL) optimum temperature, pressure and solution chemistry

conditions have been proposed as indicated in Table 2-3. These high pressure and temperature conditions have been cited as energy intensive (Huijgen and Comans, 2003).

Impact of Solution Chemistry

The initial studies in direct aqueous mineral carbonation made use of distilled water as the CO_2 carrying aqueous component (O'Connor et al., 2000). Work conducted at the Albany Research Center by O'Connor et al. (2002) showed that the use of sodium bicarbonate ($NaHCO_3$) and sodium chloride (NaCl) significantly improved the reaction rate of the carbonation reaction. They postulated that the presence of sodium bicarbonate buffered the pH of the solution at ~7.9, and also provided carbonate ions that react with the silicate mineral to produce magnesite. The sodium chloride was believed to facilitate the formation of chloride complexes with Mg^{2+} cations. This reduced the concentration of the cations in solution, thus aiding further dissolution of the silicate mineral (O'Connor et al., 2000; O'Connor et al., 2005; Bodenan et al., 2014). As a result, the conversion of serpentine increased from 57% in 24 hours in distilled water to 82% in 0.64 M $NaHCO_3$ and 1 M NaCl solution.

In a comprehensive study, adopting the methods developed by O'Connor et al. (2000), Gerdemann et al. (2007) used distilled water and NaCl/$NaHCO_3$ solutions for the mineral carbonation of olivine, wollastonite and serpentine in a direct aqueous mineral carbonation process. Their findings confirmed the observations of O'Connor et al. (2000), although they reported that carbonation of the Ca-silicate mineral, wollastonite, was independent of the solution used, as similar results were obtained for distilled water and NaCl/$NaHCO_3$ solutions. However, solution chemistry was found to have an effect on olivine and serpentine carbonation. The maximum carbonation of olivine (> 80%) and serpentine (~ 65%) was attained when NaCl/$NaHCO_3$ solution was used. The results of these studies are summarised in Table 2-3.

Table 2-3: Optimum carbonation conditions, by mineral (Adapted from Gerdemann et al., 2007)

	carbonation conditions		
Mineral	**T, °C**	**P_{CO2}, atm**	**carrier solution**
olivine	185	150	0.64 M $NaHCO_3$, 1 M NaCl
wollastonite	100	40	distilled water
HT serpentine	155	115	0.64 M $NaHCO_3$, 1 M NaCl

Though the extents of carbonation attained in this study were relatively high, it important to note that these results were obtained under high temperatures (150 °C) and pressure (150 atm P_{CO_2}). These conditions may result in severe energy penalties if adopted in industrial mineral carbonation processes.

The use of sodium salts that enhance the dissolution reaction has also been explored by researchers, in this process scheme, and improvements of up to 100% dissolution of magnesium in serpentine in 0.1 M solutions of sodium citrate, sodium EDTA and sodium oxalate have been reported (Krevor and Lackner, 2009). Though this could be an option in terms of the dissolution of serpentine-based feedstocks, the impact of these reagents on the carbonation reaction is unclear, since carbonation is favoured by alkaline conditions.

Impact of Mineral Type and Particle Size

The results of the study by Gerdemann et al. (2007), summarised in Table 2-3 above, have indicated that optimal conditions are very mineral specific, with carbonation of wollastonite being optimum at much lower temperatures and pressures, and without reagent use in comparison to olivine and heat treated serpentine. Figure 2-4 shows that more than 85% of olivine was converted to carbonate in a direct aqueous mineral carbonation process carried out at 185 °C and 150 atm CO_2 using $NaCl/NaHCO_3$ solution. In comparison, serpentine reactivity was very low, and only improved to just over 60% with heat treatment of the serpentine samples, to remove chemically bound water (Gerdemann et al., 2007).

A decrease in particle size has been demonstrated to improve the reactivity of the silicate mineral for direct aqueous carbonation (O'Connor et al., 2001; Gerdemann et al., 2002). Studies conducted by O'Connor et al. (2001) indicated a substantial increase in carbonation with a reduction of particle size from minus 75 microns to minus 35 microns.

Reducing the particle size increases the surface area of silicate mineral available for reaction, in turn increasing the reaction rate (Gerdemann et al., 2007). However, particle size reduction can incur considerable energy penalties, with Gerdemann et al. (2002) reporting an energy penalty of about 230-240 KW/ton of mineral for size reduction below 75 microns.

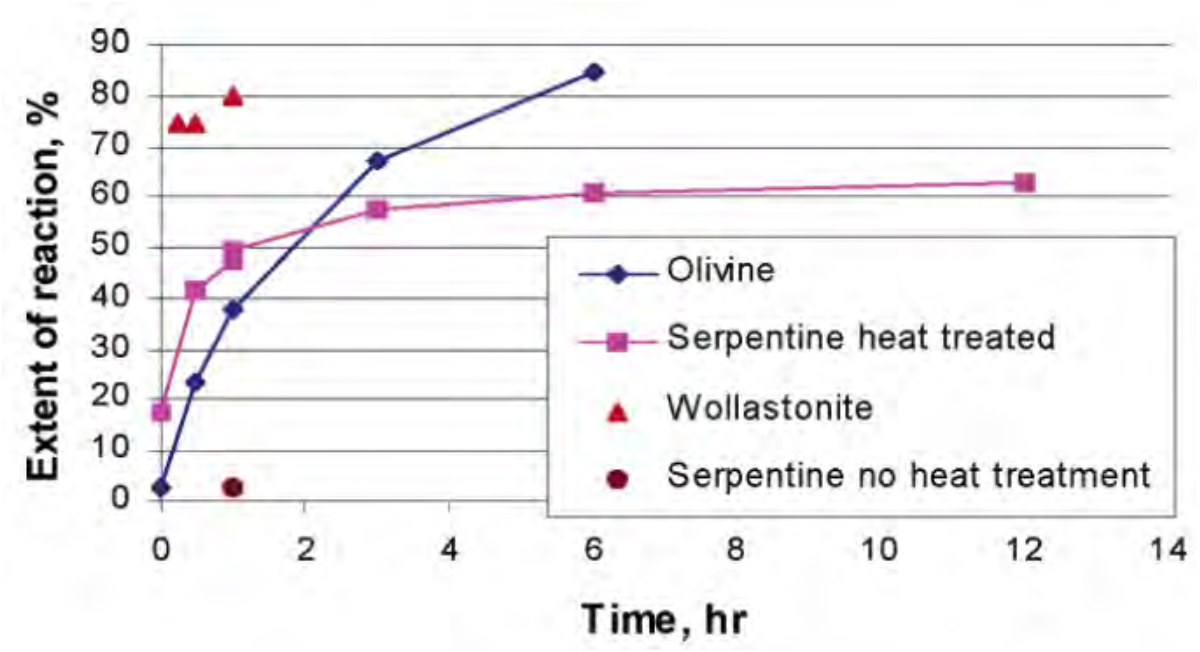


Figure 2-4: Extent of carbonation of olivine, wollastonite and serpentine at 185 °C and 150 atm CO_2 in NaCl/$NaHCO_3$ solution (Gerdemann et al., 2007)

Though heat treatment significantly increased the extent of reaction, the heat treated serpentine could not exceed 65% conversion under the same operating conditions as shown in Figure 2-4. It can also be seen from this figure that wollastonite was found to be relatively more reactive in comparison to the other silicate minerals. Koukouzas et al. (2009) used dunite, hartzburgite and pyroxenite in an aqueous mineral carbonation scheme at 155 °C and 158.6 bar using NaCl/$NaHCO_3$ solution. Though these conditions were similar to those used by Gerdemann et al. (2007), the authors reported lower (<10%) extents of carbonation for the samples studied, with pyroxenite not carbonating at all (Koukouzas et al., 2009).

2.1.3 Indirect Aqueous Mineral Carbonation

This route involves at least two separate aqueous process steps carried out in different reactors. In its simplest and most generic form, the indirect aqueous mineral carbonation approach entails the reaction of aqueous solutions with silicate minerals to convert them to more reactive forms, specifically soluble cations or hydroxide compounds (mineral conversion), followed by the reaction with carbon dioxide to form stable mineral carbonates. The most attractive of these processes are those that provide for regeneration of the conversion reagent (Figure 2-5).

The biggest advantage of the indirect, multi-stage mineral carbonation approach is that it allows for individual optimisation of process steps, in isolation.

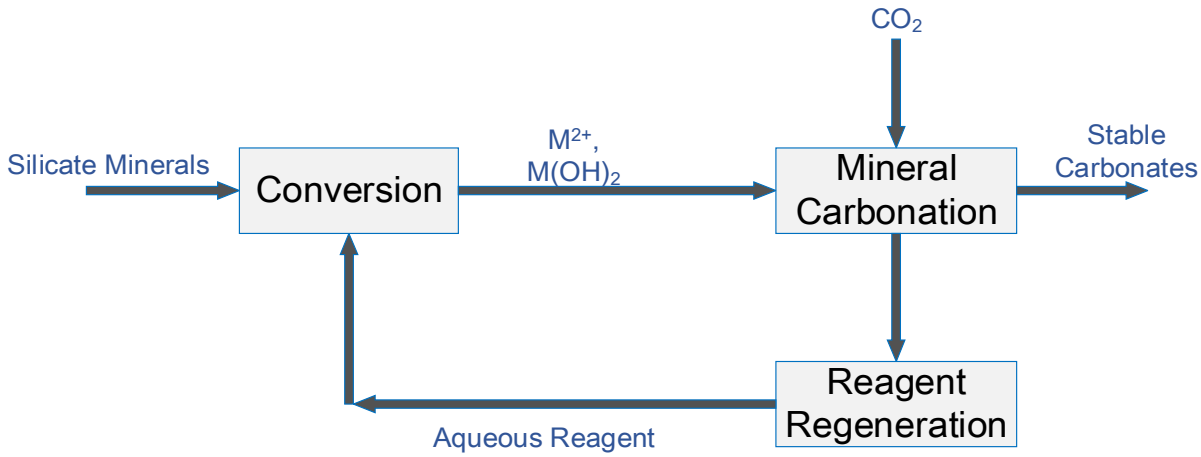


Figure 2-5: Generic indirect aqueous carbonation approach

The indirect aqueous processes reviewed here include the generic pH swing method, the ammonium salts process, which is a hybrid of the pH swing method, Lackner's multi-stage process (based on HCl extraction), the acetic acid process, and the alkali leach process.

pH Swing Method

The aqueous carbonation of silicate minerals is a two-step process that involves; 1) the dissolution of cations into solution under acidic conditions, and 2) the carbonation of dissolved cations in the solution under alkaline conditions. The pH swing method, is based on studies by Park et al. (2003) which established that the overall carbonation rate was limited by the extent of carbonic acid dissociation into bicarbonate or carbonate ions in acidic conditions. These acidic conditions enhanced the dissolution of the silicate mineral but inhibited the carbonation of magnesium ions. The carbonation reaction was favoured by high pH conditions, with the optimum pH being around 10 (Park, 2005). It was from this understanding that the authors proposed the pH swing method. The first step of the pH swing method entails the extraction of cations from the silicate minerals through dissolution, typically, in inorganic acids, organic acids, or a mixture of the two (Park and Fan, 2004; Teir et al., 2007a; Meyer et al., 2014), although ammonium salts have also been used (Wang and Maroto-Valer, 2011; Sanna et al., 2014a). The acidic leach solution is then pH adjusted using alkaline solutions such as sodium hydroxide, and subsequently carbonated with CO_2 (Meyer et al., 2014).

A schematic illustration of a pH swing process is provided in Figure 2-6, and a detailed review of the mineral dissolution (extraction) and carbonation steps outlined in the sub-sections below.

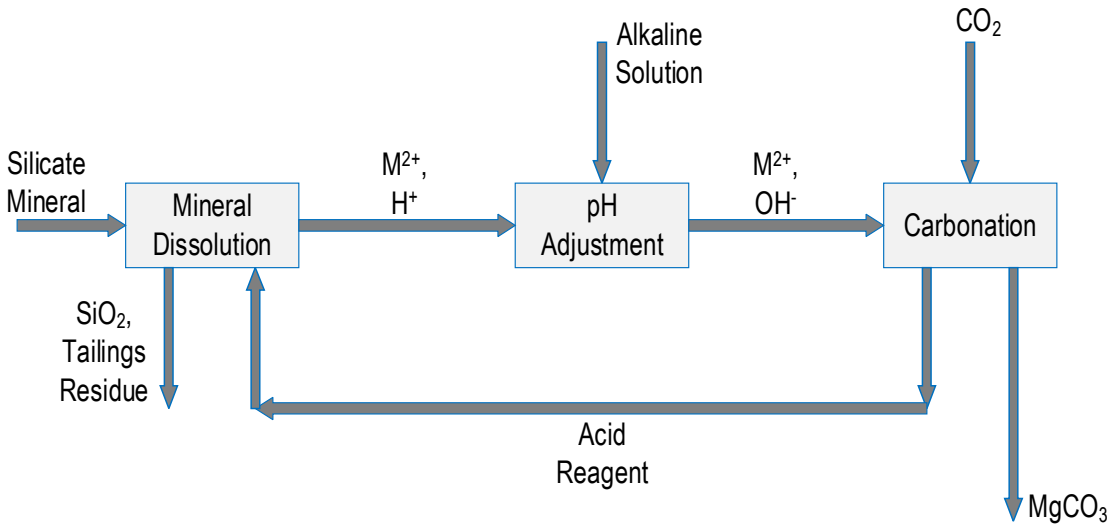


Figure 2-6: Simplified schematic of pH swing process

Mineral Dissolution

The extraction of cations from the mineral matrix is the first step in indirect aqueous carbonation, and indeed, in the pH swing method. This step has also been identified as rate limiting (Park and Fan., 2004; Alexander et al., 2007; Gerdemann et al., 2007; Meyer et al., 2014), and accordingly much of the research and development in this area has been focused on accelerating this step. A number of parameters affect the extraction of alkaline earth metals from the silicate minerals including solution chemistry, temperature and pressure conditions, mineral type and particle size.

i. Solution Chemistry

An important parameter that affects the indirect aqueous mineral carbonation process is the solution chemistry, particularly for the extraction of the metal cations from the silicate mineral matrix. Researchers have thus experimented with different chemical reagents, from organic to inorganic acids, to ammonium salts, as well as alkaline solutions among others. Depending on the pH, the extraction of the silicate mineral can either be proton controlled, at low pH (Krevor and Lackner, 2001) or be enhanced by the presence of ligands that weaken or polarize the bond between the cation and the mineral lattice, at pH conditions near neutral (Brantley, 2008). This occurs when the protons from the organic acid hydrate the Si-O tetrahedral, with the ligands forming complexes at the reaction front through covalent bonding between the oxygen of the organic compound and the surface metal (Meyer, 2014). Table 2-4 is a summary of results from

the extraction of various silicate minerals using different solutions; organic and inorganic acids, mixtures of the two, as well as ammonium salts.

Table 2-4: Summary of results from dissolution studies

Study	Silicate Mineral	Solvent	Extraction efficiency
Park and Fan (2004)	Serpentine	A mixture of H_3PO_4, oxalic acid and EDTA	65% in 1 hr
		Ammonium Bisulphate (NH_4HSO_4)	42% in 1 hr
Teir et al. (2007)	Serpentinite	Acid Solutions (HCl,H_2SO_4,HNO_3,$HCOOH$,CH_3COOH)	3-26% in 1 hr
		Alkaline Solutions ($NaOH$,KOH,NH_3)	<0.05% in 1 hr
		Ammonium Salt Solutions (NH_4Cl,$(NH_4)_2SO_4$,NH_4NO_3)	0.3-0.5% in 1 hr
Wang and Maroto-Valer (2011)	Serpentine	Ammonium Bisulphate (NH_4HSO_4)	>50% in 3 hrs
		Ammonium Chloride (NH_4Cl)	<5% in 3 hrs
		Ammonium Sulphate ($(NH_4)_2SO_4$)	<5% in 3 hrs
		Sulphuric Acid (H_2SO_4)	~45% in 3 hrs
Meyer et al. (2014)	PGM Tailings	A mixture of HCl, oxalic acid and EDTA	<4.5% in 5 hrs
		Hydrochloric Acid (HCl)	<5% in 8 hrs
Meyer (2014)	enstatite	0.1 M HCl	<2.1% in 48 hrs
	augite		<14% in 48 hrs
	diopside		3.3% in 48 hrs

In one of the initial studies in this approach, Park and Fan (2004) investigated the dissolution of serpentine in a fluidized reaction system with internal grinding. The solvents used were 1.4 M ammonium bisulphate (NH_4HSO_4) and a mixture of acids (1 vol% H_3PO_4, 0.9 wt% oxalic acid and 0.1 wt% EDTA solution). Ambient pressure and moderate temperature (70 °C) conditions were used by the authors (Park and Fan, 2004). The researchers reported that mixture of acids was more effective at leaching magnesium resulting in a 65% extraction efficiency in comparison to 42% extraction achieved using the 1.4 M solution of ammonium bisulphate. Teir et al. (2007a) investigated the effect of different concentrations (1 M, 2 M, 4 M) of various solvents on the extraction of magnesium from a 74-125 μm sample of serpentinite at temperatures of 30 °C, 50 °C and 70 °C. The solvents they considered included inorganic acids (H_2SO_4, HCl, HNO_3), organic acids (HCOOH, CH_3COOH), alkaline solutions (NaOH, KOH, NH_3), as well as various ammonium salts (NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3). Their findings, summarised in Figure 2-7, demonstrated that H_2SO_4 was the most effective solvent for the dissolution of serpentinite.

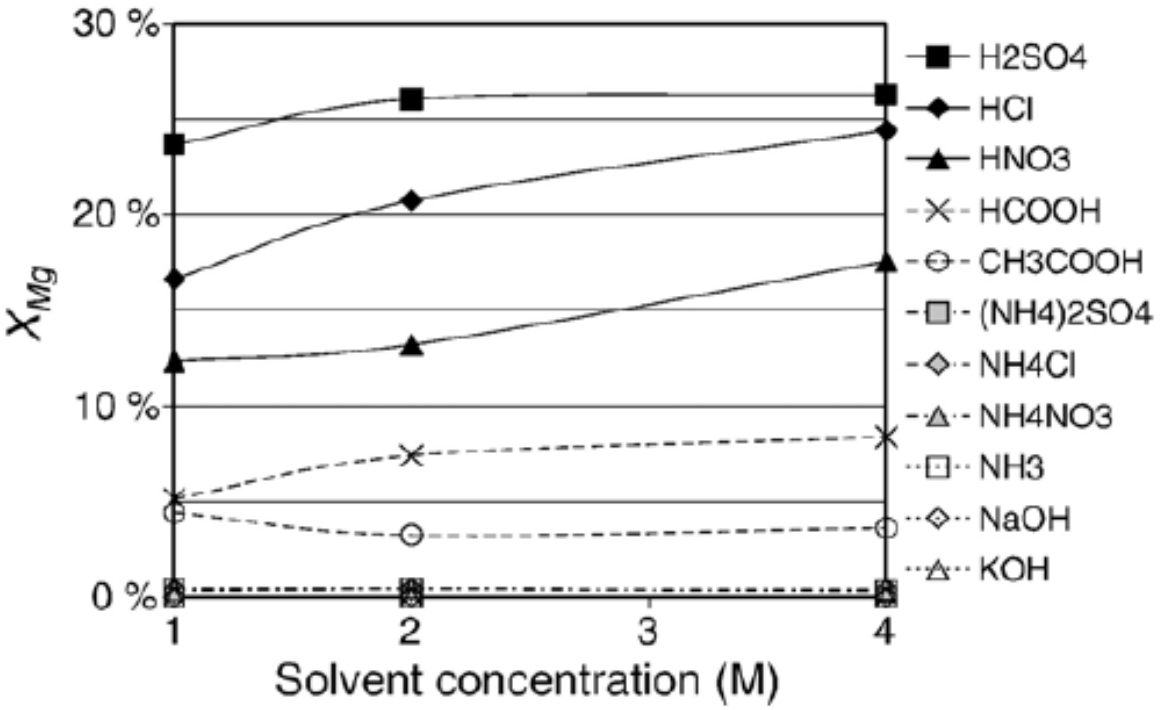


Figure 2-7: Extraction efficiency of magnesium from serpentinite in 1 M, 2 M, 4 M solutions at 20 °C in 1 hr (Teir et al., 2007a)

Overall, the study found the most effective solvents were inorganic acids followed by organic acids. Ammonium salts, though selectively extracting magnesium, had lower extraction ratios. Finally, the alkaline solutions tested yielded no measureable amount of cation extraction. In their work Teir et al. (2007) constrained the dissolution experiments to a 1-hour timeframe. The use of longer time-frames (≥ 6 hours) would have been more illuminating, especially with regard to the selectivity of ammonium salts.

A study by Wang and Maroto-Valer (2011) compared the rate of extraction of magnesium from serpentine using $(NH_4)_2SO_4$, NH_4Cl and NH_4HSO_4, and H_2SO_4 under different conditions. The use of H_2SO_4 was to compare the performance of the ammonium salts against a strong inorganic acid that was effective in mineral dissolution (Teir et al., 2007). The use of ammonium salts provides opportunities to recycle dissolution reactants (Maroto-Valer and Wang, 2011). Results, summarised in Figure 2-8, indicated that ammonium bisulphate (NH_4HSO_4) extracted the most magnesium from serpentine at 70 °C in 3 hours (50%), followed by H_2SO_4 (45%). NH_4Cl and $(NH_4)_2SO_4$ resulted in low extraction efficiencies (<5% Mg extraction). The results obtained by Wang and Maroto-Valer (2011) were consistent with those obtained by Teir et al (2007a) and Park and Fan (2004).

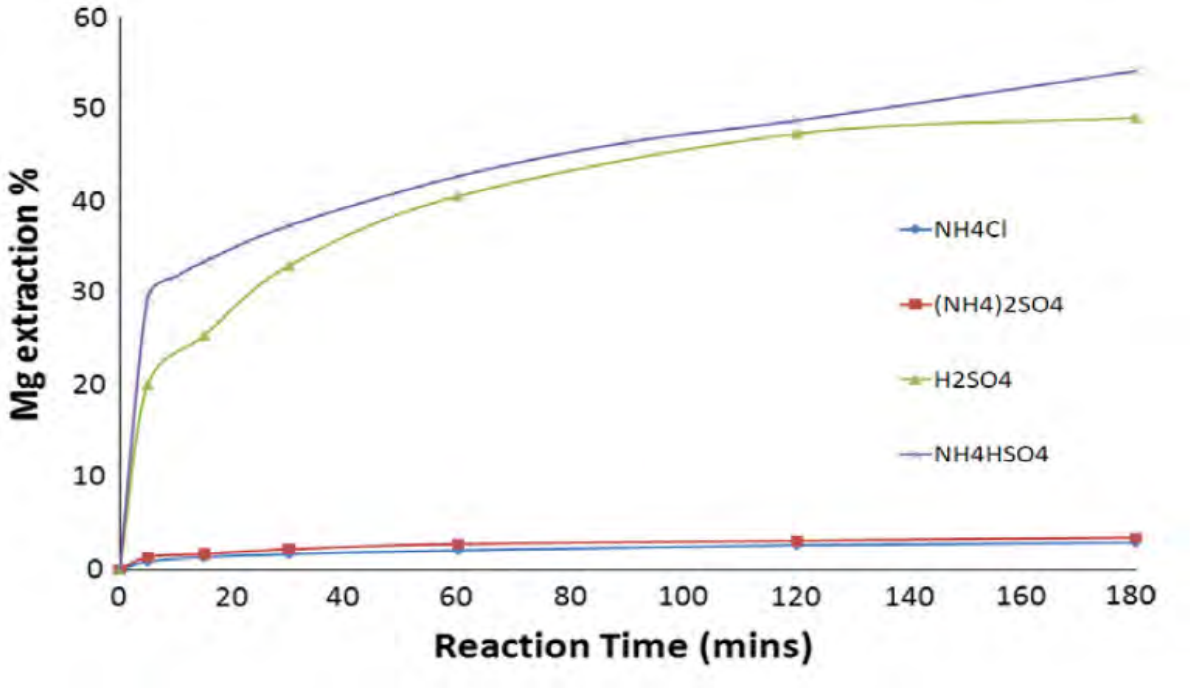


Figure 2-8: Extraction efficiency of magnesium from serpentinite in ammonium salt and sulphuric acid solutions at 70 °C in 3 hrs (Wang and Maroto-Valer, 2011)

It is important to note that 2 M NH_4HSO_4 was used in the study by Wang and Maroto-Valer (2011) in comparison to the 1.4 M NH_4HSO_4 solvent used by Park and Fan (2004), which suggests that extraction of cations is independent of acid concentration at these molarities for this particular solvent.

To investigate the mineral carbonation of pyroxene-rich PGM tailings, Meyer et al. (2014) used an inorganic acid (2 M HCl) and mixtures of 0.06-0.09 M hydrochloric acid, 0.01-0.04 M EDTA and 0.001-0.1 M oxalic acid for dissolution at 70 °C. The authors noted that this mixture of acids solvent did not increase extraction of magnesium as reported by Park et al. (2003).

Temperature

In dissolution studies by Teir et al., (2007a) discussed in (*i*) the researchers also conducted experiments to determine the effect of temperature on extraction. The authors reported an increase in magnesium dissolution from serpentinite with an increase in temperature from 30 °C to 70 °C using 2 M solutions of sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3). Figure 2-9 shows the effect of temperature on the dissolution of magnesium and iron in 2 M H_2SO_4 solution. It is noted that 100% extraction of magnesium was obtained at 70 °C. Similar results were also reported for HCl and HNO_3 solutions (Teir et al., 2007a).

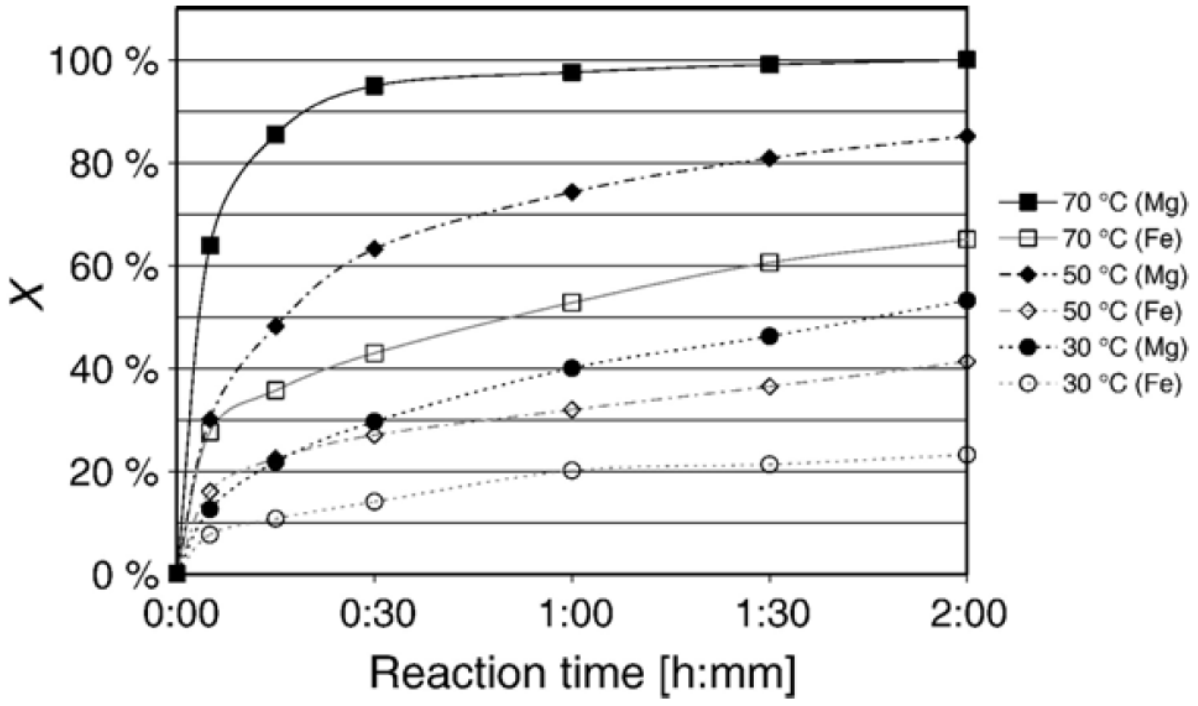


Figure 2-9: Effect of temperature on extent of dissolution of Mg and Fe in 2 M H_2SO_4 (Teir et al., 2007a)

Prigiobbe and Mazzotti (2011) investigated the effect of temperature in the dissolution of olivine in sodium salts (oxalate and citrate). They reported enhanced dissolution of olivine with increased temperatures up to 120 °C, demonstrated by the increase in the specific dissolution rate. Another author in the same research group, Hanchen et al. (2006), had earlier conducted dissolution experiments on olivine (forsterite end-member), using hydrochloric acid at temperatures from 90-150 °C. Their results also indicated an increase in dissolution with an increase in temperature, with dissolution rates of 2.2e-10 to 3.76e-9 $mol \cdot cm^{-2} \cdot s^{-1}$ at temperatures of 90 °C and 150 °C, respectively.

Alexander et al. (2007) reported a 70% increase in magnesium extraction from serpentine by sulphuric acid with an increase in temperature from 25 °C to 50 °C, whilst studies by Wang and Maroto-Valer (2011) showed that magnesium extraction efficiencies in a 1.4 M ammonium bisulphate solution increased, on increasing the temperature in the range 70 °C to 100 °C. In accordance with the latter studies, summarized in Figure 2-10, the effect of temperature becomes more pronounced at higher temperatures, with the extraction efficiency approaching 100% at 100 °C.

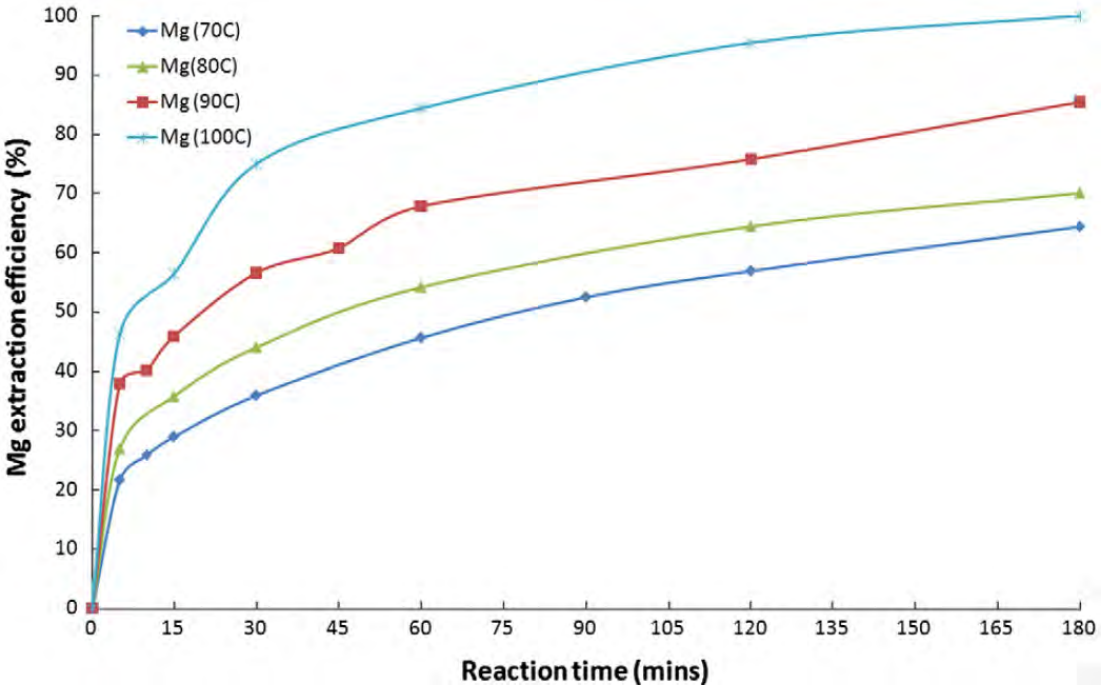


Figure 2-10: Effect of temperature on the dissolution of serpentine in 1.4 M NH_4HSO_4 solution (Wang and Maroto-Valer, 2011)

A similar study conducted by Sanna et al. (2014a) on pyroxene in 1.4 M ammonium bisulphate exhibited similar, though more modest increases in extraction efficiencies on increasing the temperature from 50 °C to 100 °C (Figure 2-11).

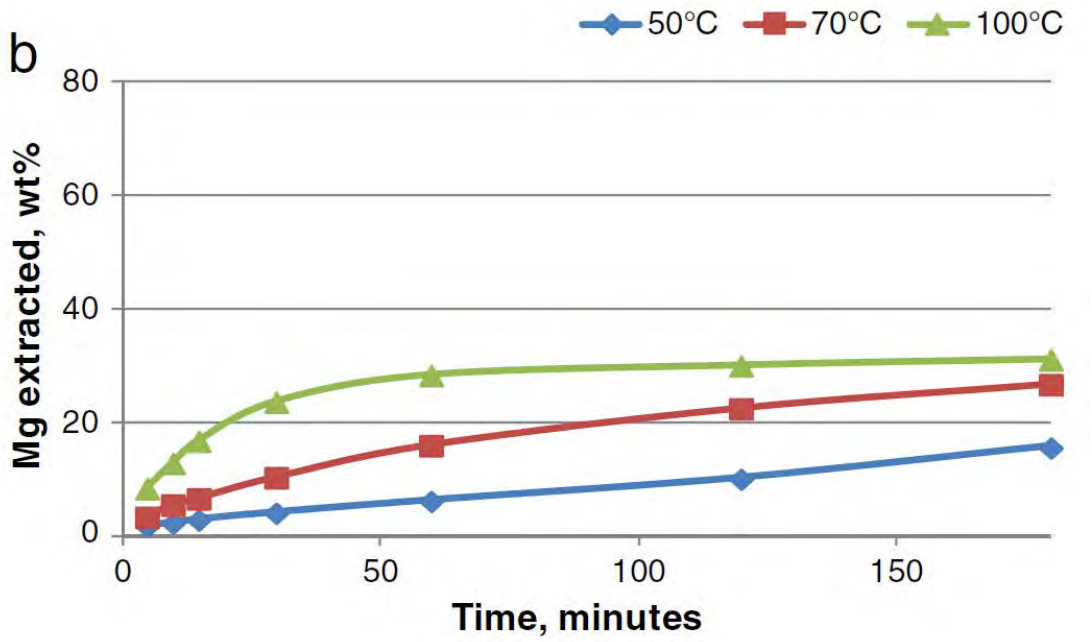


Figure 2-11: Effect of temperature on the dissolution of pyroxene in 1.4 M NH_4HSO_4 solution (Sanna et al., 2014a)

ii. Mineral Type

A review of results indicates that the rate and extent of dissolution is highly dependent on the structure, and hence type of mineral (see results in Table 2-5).

Table 2-5: Impact of mineral type on magnesium extraction under the same conditions

Study	Silicate Mineral	Solvent	Conditions	Mg-Extraction efficiency
Sanna et al. (2014)	Olivine	1.4 M NH_4HSO_4	100 °C, 1 atm	78% in 3 hrs
	Pyroxene			31% in 3 hrs
	Amphibole Rocks			29% in 3 hrs
Meyer (2014)	enstatite	0.1 M HCl	40 °C, 1 atm	<2.1% in 48 hrs
	augite			<14% in 48 hrs
	diopside			3.3% in 48 hrs

The study by Sanna et al. (2014a) showed that olivine was considerably more reactive than pyroxene and amphibole-rich rocks, with a 1.4 M bisulphate solution resulting in Mg-extraction of 77% from olivine in 3 hours at 100 °C compared to approximately 30% Mg-extraction from pyroxene and amphibole under the same conditions. In accordance with the study by Meyer (2014) reactivity of silicate minerals in dilute HCl solutions at 40 °C decreased in the order, wollastonite > diopside = augite > enstatite. Meyer attributed this reactivity to the structure of the minerals, particularly in terms of the length of the metal-oxygen bonds and the size and location of the metal cations in the mineral structure (Meyer, 2014). In order to increase Mg-extraction in pyroxene samples researchers have suggested the application of mechanical activation, higher temperatures and pressures, exploring different leach reagents as well as increased reaction times (Koukouzas et al., 2009; Meyer et al., 2014). These tailings are mostly orthopyroxene (65 wt.%) and plagioclase (16 wt.%) with clinopyroxene and amphibole in smaller amounts (Meyer et al., 2014). The authors obtained relatively low extraction of magnesium (<4.8%) in comparison to that reported by other authors using similar solvents to extract cations from more reactive serpentine minerals (Park and Fan, 2004; Teir et al, 2007a; Wang and Maroto-Valer, 2011). Meyer (2014) conducted dissolution experiments on pure pyroxene minerals (augite, wollastonite, enstatite and diopside), at temperatures between ambient and 70 °C, using 0.1 M hydrochloric acid. The extraction efficiency of magnesium in all these minerals was reported to be low, with the highest attained efficiency being 12% extracted from augite.

Carbonation

The next major process step in the pH swing method, is the carbonation of cations in solution, under alkaline conditions. Park and Fan (2004) used ammonium hydroxide (NH_4OH) to increase the pH to 9.5, at which point the precipitation of magnesium carbonate occurred at ambient temperature conditions. According to these researchers, the precipitation of magnesium carbonate was instantaneous at the desired alkaline pH conditions resulting in complete conversion of the dissolved magnesium in solution in both solvent cases. In their studies, Teir et al. (2007b) used sodium hydroxide (NaOH) to adjust the pH, to an optimum carbonation pH of 9. The authors reported carbonation efficiencies of up to 94% at 30 °C, producing a hydromagnesite product that is up to 99% pure. Meyer et al. (2014) also used the same pH conditions and chemical reagent (NaOH) in carbonation of cation solutions produced through dissolution by 2 M HCl. The authors reported "rapid and efficient" carbonation under these conditions. Wang and Maroto-Valer (2013) reported carbonation efficiencies of more than 90% at 80 °C using ammonium bicarbonate, produced from carbon dioxide capture with NH_4OH to carbonate the cation solution.

Case Study Examples of the two-stage pH swing process

Implementing the pH swing method to their work on serpentinite, a rock primarily dominated by serpentine group minerals, Teir et al. (2007b) conducted dissolution experiments using solutions of hydrochloric acid and nitric acid at 70 °C (Equations 13 and 14).

$$Mg_3Si_2O_5(OH)_{4(s)} + 6HCl_{(aq)} \rightarrow 3MgCl_{2(aq)} + 2SiO_{2(s)} + 5H_2O_{(l)} \quad (13)$$

$$Mg_3Si_2O_5(OH)_{4(s)} + 6HNO_{3(aq)} \rightarrow 3Mg(NO_3)_{2(aq)} + 2SiO_{2(s)} + 5H_2O_{(l)} \quad (14)$$

The authors found relatively high extraction efficiencies for both hydrochloric acid and nitric acid at 92.6% and 88.3%, respectively. The dissolution experiments were followed up by further testwork to establish the optimum pH for the precipitation of magnesium ions into carbonate through carbonation at 30 °C and 1 atm. The leach solutions produced were carbonated at varied pH conditions and the optimum carbonation pH was reported to be pH 9, which gives the highest amount of carbon dioxide fixed as carbonate as indicated in Figure 2-12. From this figure it can be also seen that this pH also provided the highest purity of hydromagnesite (99%).

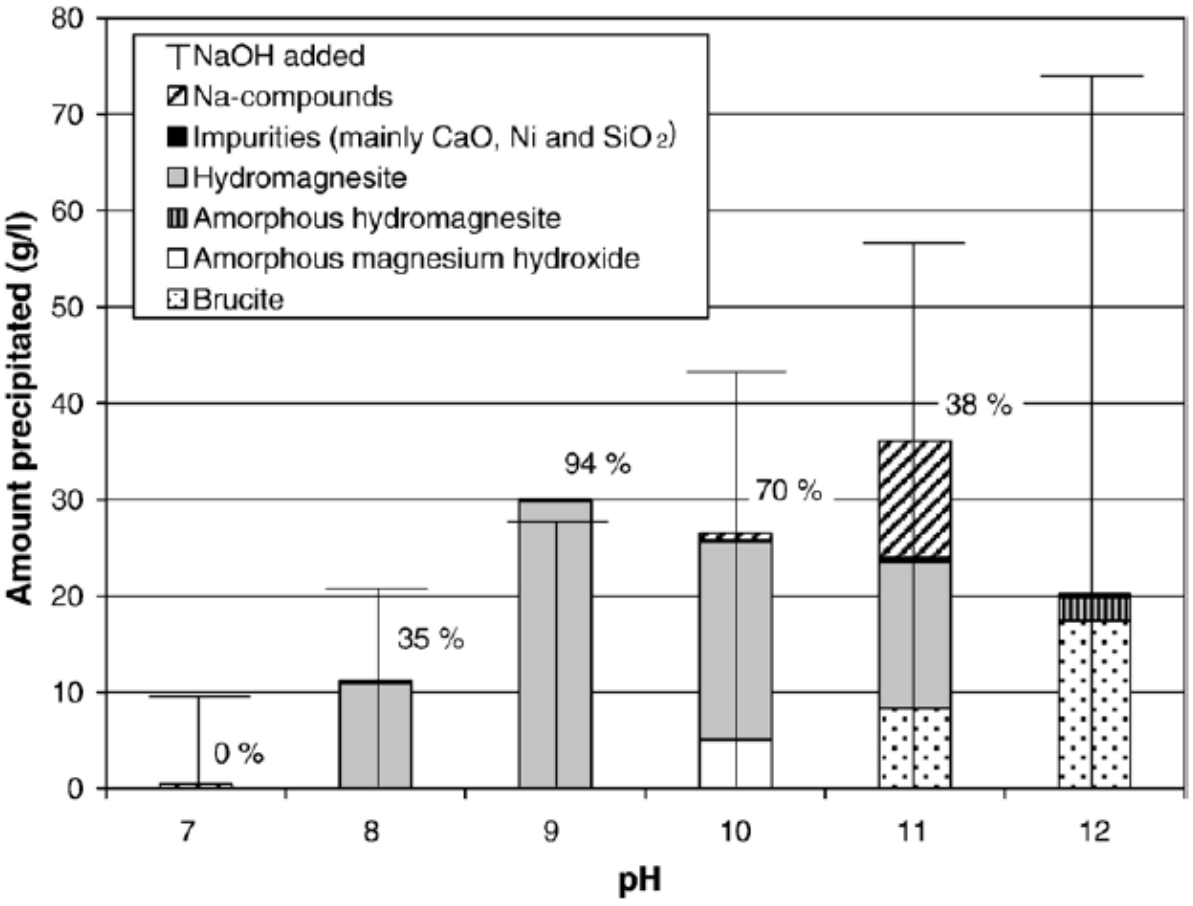


Figure 2-12: Results from the conversion of magnesium ions into carbonate, effect of pH (Teir et al., 2007b)

This work served as a basis for the development of a conceptual plant for the mineral carbonation of serpentinite (Teir et al., 2009). Upon dissolution the authors proposed the evaporation of water to crystallise the nitrate and chloride salts of magnesium (Teir et al., 2007b; Teir et al., 2009). The addition of sodium hydroxide and water dissolves the salts and neutralises the solution, also precipitating any iron oxides present. The solution is finally carbonated to produce hydromagnesite through the addition of more sodium hydroxide and bubbling carbon dioxide through the solution. A simple flowsheet for the proposed process is presented in Figure 2-13. The authors found it would require 3.1 tons of serpentine to store a ton of carbon dioxide. It was also found that significant quantities of acid and sodium hydroxide are required, and that potential recycling of these reagents could require energy intensive operations like electrolysis (Teir et al., 2009).

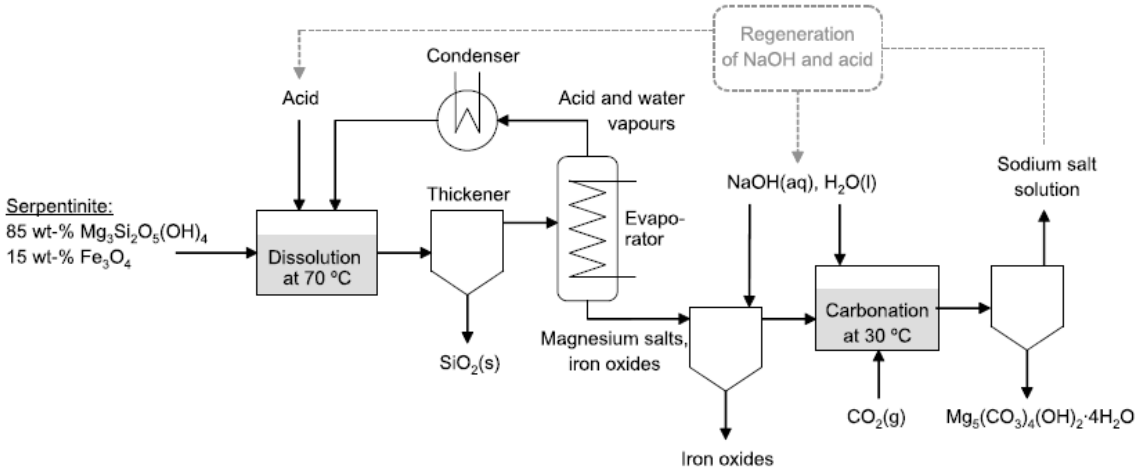


Figure 2-13: A simple flowsheet for the carbonation of serpentinite through a pH swing method using HCl/HNO3 and NaOH (Teir et al., 2009)

A similar approach was taken in studies conducted on pyroxene-rich PGM tailings (Vogeli, 2012; Meyer et al., 2014). The authors adopted the pH swing process to the dissolution and carbonation of cations in pyroxene-rich PGM tailings. After a classification study to ascertain the potential of PGM tailings to sequester carbon dioxide, Vogeli (2012) used 2 M hydrochloric acid to leach different samples of PGM tailings at 70 °C. The resulting leach solution was subsequently pH adjusted to pH 9 using 15 M sodium hydroxide prior to carbonation at 20 °C. In contrast to the process proposed by Teir et al. (2007), the evaporation of the acid solution for recycle prior to pH adjustment was not part of this approach. Comparatively modest extraction efficiencies were reported (~20%) in comparison to other silicate minerals studied under the same conditions, as reported by Teir et al. (2007b) discussed earlier. The carbonation efficiency of the pH adjusted leach solution was reported to range between 48% and 69% (Vogeli, 2012). Meyer et al. (2014) reported findings that reaffirmed observations that mineral dissolution is the rate limiting step in aqueous mineral carbonation (Park and Fan, 2004; Wang and Maroto-Valer, 2011; Bonfils et al., 2012) since subsequent carbonation was "rapid and efficient".

The Ammonium Salts Process

In a modified version of the pH-swing method, Wang and Maroto-Valer (2011) proposed a multi-stage ammonium salts process to capture carbon dioxide, extract and carbonate the silicate mineral. This process was developed based on a patent for the production of silica, iron oxide and magnesium carbonate from serpentine wastes for economic purposes (Pundsack et al., 1967). The process is described below through key chemical equations and operations, and presented schematically in Figure 2-14:

1. *CO_2 Capture*: The ammonium salts process integrates carbon dioxide capture from flue gases as part of the carbonation process. Hydrated ammonia is used to capture ambient pressure carbon dioxide producing ammonium bicarbonate at 10 °C. This is claimed to have the benefit of resulting in energy savings by avoiding compression and transport of carbon dioxide (Wang and Maroto-Valer, 2011).

$$NH_{3(g)}+CO_{2(g)}+H_2O_{(l)}\rightarrow NH_4HCO_{3(aq)} \quad (12)$$

2. *Mineral Dissolution*: A 1.4 M solution of ammonium bisulphate is then used, in excess of 40%, as the leaching agent to extract magnesium from serpentine at 90 °C, producing a solution of magnesium and ammonium sulphate as well as solid silicon dioxide. This, the authors assert, enables the recovery of pure silica which can be of commercial benefit (Wang et al., 2013).

$$Mg_3Si_2O_5(OH)_{4(s)}+6NH_4HSO_{4(aq)}\rightarrow 3MgSO_{4(aq)}+2SiO_{2(s)}+5H_2O_{(l)}+3(NH_4)_2SO_{4(aq)} \quad (13)$$

3. *pH adjustment*: Since 40% excess ammonium bisulphate is used in the dissolution step, ammonium hydroxide is added to neutralise this excess acid at 25 °C. The product of this reaction is ammonium sulphate, which can be decomposed to reproduce key reagents in the process.

$$NH_4HSO_{4(aq)}+NH_4OH_{(aq)}\rightarrow (NH_4)_2SO_{4(aq)}+H_2O_{(l)} \quad (14)$$

4. *Carbonation*: Using ammonium carbonate from the capture step as the CO_2-carrier, magnesium sulphate leach solution is carbonated at 80 °C to produce hydromagnesite.

$$MgSO_{4(aq)}+2NH_4HCO_{3(aq)}+2H_2O_{(l)}\rightarrow MgCO_3\cdot 6H_2O_{(s)}+(NH_4)_2SO_{4(aq)}+CO_{2(g)} \quad (15)$$

5. *Reagent Regeneration*: Some preceding process steps (dissolution, pH adjustment, carbonation) in the process produce ammonium sulphate in solution. To regenerate chemical reagents, the water is evaporated leaving behind solid ammonium sulphate crystals. Solid ammonium sulphate is then thermally decomposed (T>300 °C) evolving gaseous ammonia and leaving behind an ammonium bisulphate solid residue (Wang, 2011). These can then be recycled for use in the capture and dissolution steps, respectively.

$$(NH_4)_2SO_{4(s)}\rightarrow NH_4HSO_{4(s)}+NH_{3(g)} \quad (16)$$

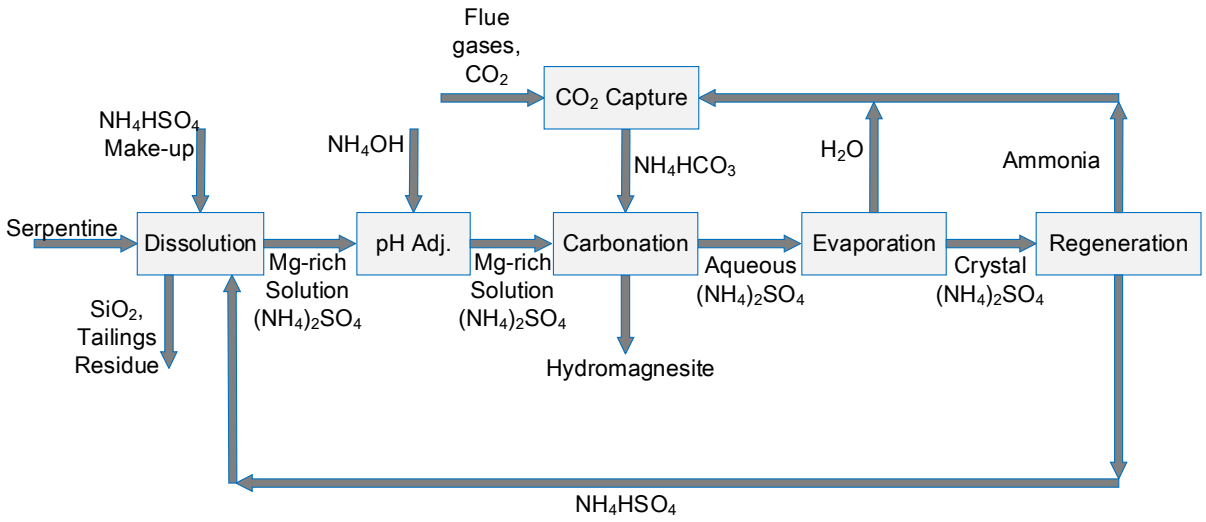


Figure 2-14: Process schematic of recyclable ammonium salts process (adapted from Wang and Maroto-Valer, 2013)

The researchers have reported magnesium extraction efficiencies of up to 100% from serpentine at 100 °C in 3 hours, and carbonation efficiency of up to 95.9% through laboratory conducted experiments (Wang et al, 2013). This signifies potential for the recyclable ammonium salts process, in that it also integrates CO_2 capture. However, the recovery of reagents through thermal decomposition has potential to incur substantial energy penalties. The requirement of prior removal of water to crystallize ammonium sulphate and the high temperatures required in the endothermic decomposition reaction is concerning from an energy perspective.

Lackner's Multi-stage Process

Based on a process developed during World War II, this method involves the use of hydrochloric acid to extract metal cations from the mineral matrix. The cations are then converted to more reactive hydroxides which are then reacted with gaseous CO_2. This approach was first proposed by Lackner et al. (1995) for the purposes of mineral carbonation. A simplified flowsheet of this process is provided in Figure 2-15. This was a conceptual process not with no known experimental work conducted by the authors to validate its feasibility.

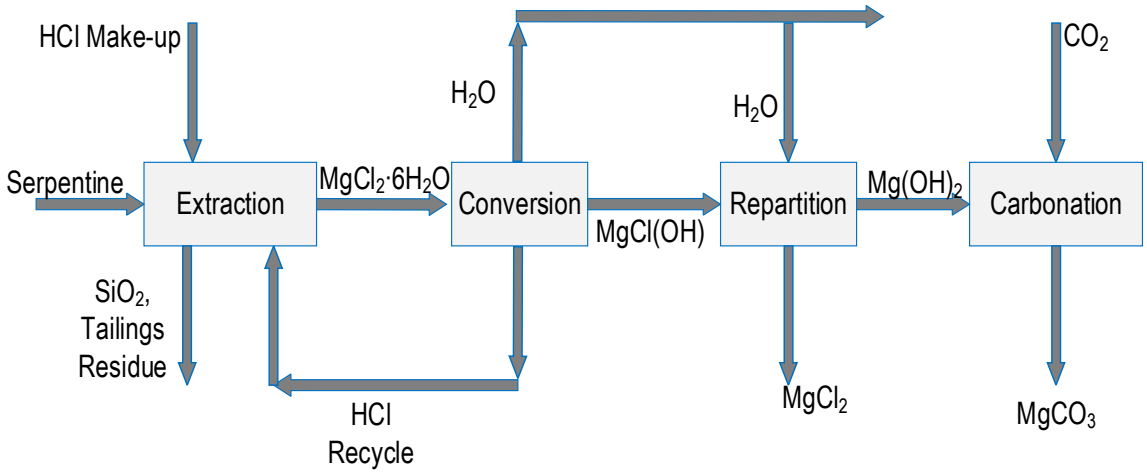


Figure 2-15: Simplified schematic of Lackner's multi-stage process

The extraction of magnesium from serpentine using HCl would proceed according to the following steps, as an example (Rackley, 2010):

Step 1: *Extraction of magnesium as $MgCl_2$ from serpentine*. The magnesium is extracted from serpentine through the use of excess hydrochloric acid to produce $MgCl_2 \cdot 6H_2O$.

$$Mg_3Si_2O_5(OH)_{4(s)} + 6HCl_{(aq)} + 13H_2O_{(l)} \rightarrow 3MgCl_2 \cdot 6H_2O_{(aq)} + 2SiO_{2(s)} \quad (7)$$

Step 2: *(Conversion) HCl recovery by heating solution to ~ 150 °C*. Hydrated magnesium chloride ($MgCl_2 \cdot 6H_2O$) is converted to MgCl(OH). Here the solution is heated to recover acid for the purposes of re-use in the first step. $MgCl_2 \cdot 6H_2O$ initially loses water resulting in $MgCl_2 \cdot H_2O$, and then eventually HCl separates instead of further water release (Lackner et al., 1995).

$$MgCl_2 \cdot 6H_2O_{(aq)} \rightarrow MgCl(OH)_{(s)} + HCl_{(aq)} + 5H_2O_{(l)} \quad (8)$$

Step 3: *(Repartition) Water introduced to convert MgCl(OH) to $Mg(OH)_2$*. Through the introduction of water MgCl(OH) is converted into solid $Mg(OH)_2$ and $MgCl_2$ solution. These are then separated and $Mg(OH)_2$ is sent for carbonation (Lackner et al., 1995).

$$2MgCl(OH)_{(s)} \rightarrow Mg(OH)_{2(s)} + MgCl_{2(aq)} \quad (9)$$

Step 4: Magnesium hydroxide is subsequently carbonated at 407 °C in an atmosphere of carbon dioxide at 1 bar.

$$Mg(OH)_{2(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)} + H_2O_{(g)} \quad (10)$$

The relative free energy changes at each major process stage are presented in Figure 2-16. This variation, due to the formation of intermediate products, has been cited as a drawback, along with the energy required for the HCl recovery step (Teir, 2008). A study conducted by Newall et al. (2000) suggested this requirement could lead to four times the amount of CO_2 produced to generate this energy compared to that sequestered by the process.

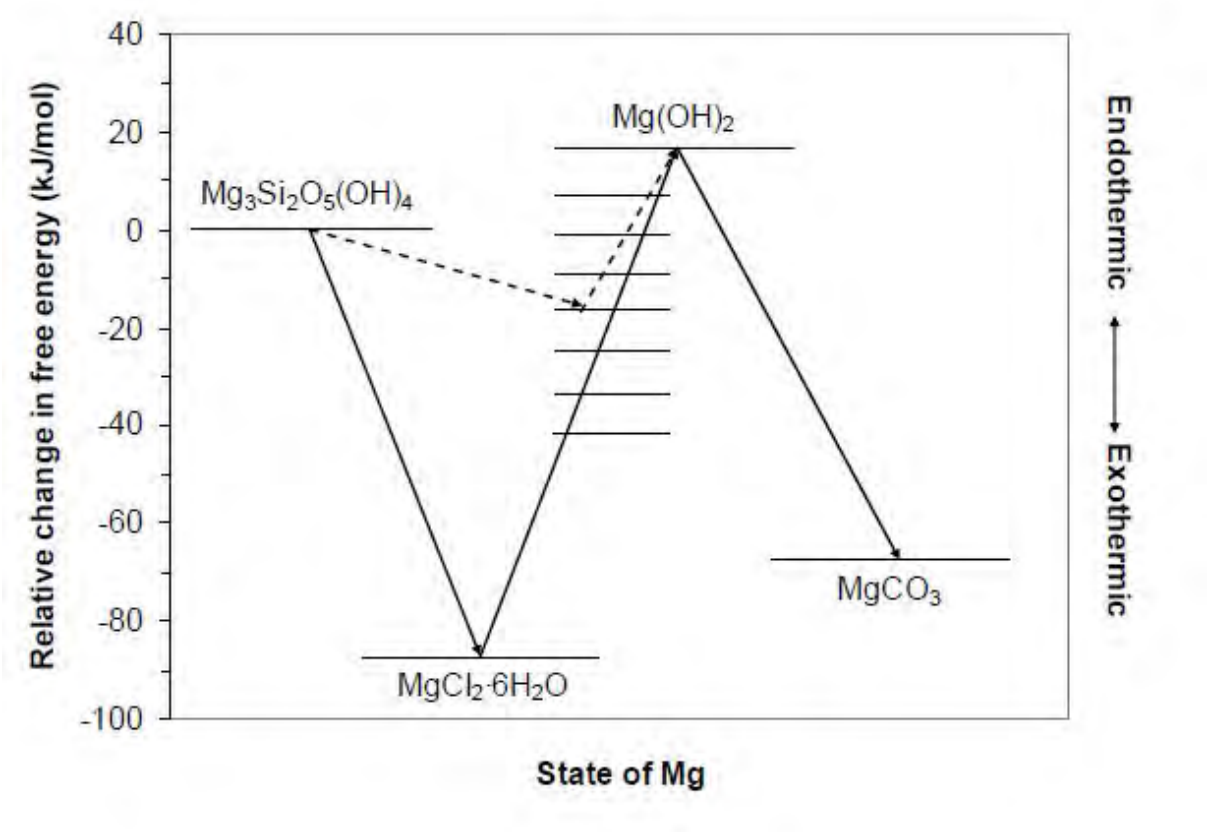


Figure 2-16: Relative free energy changes at the main process stages of the indirect carbonation (Teir, 2008)

To circumvent the high energy demand of the HCl recovery step, the use of molten melts of magnesium chloride was put forward by Wendt et al. (1998). This minimizes the energy requirement by reducing the amount of water due to application of a melt instead of hydrochloric acid for magnesium extraction. Optimum conditions for the carbonation of the silicate mineral with the melt were found to be 300 °C and 30 atm P_{CO_2}. This process would require substantial quantities of magnesium chloride which could account for a significant portion of global demand and upset the CO_2 balance for the process (Newall et al., 2000).

Maroto-Valer et al. (2005) also conducted experiments that explored the activation of the silicate mineral, serpentine, through chemical and physical means to increase the surface area, thus improve the reaction rate. This approach is similar to Lackner et al. (1995) in that the silicate mineral is converted to magnesium hydroxide, albeit using different reagents. The

authors used sulphuric acid to extract magnesium from serpentine producing magnesium sulphate at 50 °C. This was then converted to magnesium hydroxide through the use of sodium hydroxide. The resulting magnesium hydroxide was carbonated at 20 °C and 45 atm CO_2 pressure. It was reported that a carbonation efficiency of 52.5% for magnesium hydroxide was obtained (Maroto-Valer et al., 2005). These conditions are considerably milder than those used other process routes like the direct aqueous route (155 °C, 115 atm). However, the chemical make-up and energy intensive regeneration are notable concerns that could negate the benefits of this process (Sanna et al., 2014b).

Acetic Acid Process

This route has the advantage of using a less corrosive medium in comparison to strong acids like hydrochloric acid and sulphuric acid (Rackley, 2010). The process, proposed by Kakizawa et al. (2001) separates the carbonation process into two process steps. Based on the experimental data obtained by the authors, they developed the conceptual flowsheet of the process presented in Figure 2-17:

Step 1: *Dissolution*: Acetic acid solution (13.72g acid/50g water) is used to extract calcium from wollastonite, at 60 °C and atmospheric conditions, producing calcium acetate and a silica gel that can be separated through a solid-liquid separation unit.

$$CaSiO_{3(s)}+2CH_3COOH_{(l)}\rightarrow Ca^{2+}{}_{(aq)}+2CH_3COO^{-}{}_{(aq)}+H_2O_{(l)}+SiO_{2(s)} \quad (11)$$

Step 2: *Deposition and Crystallization*: In this step, through the introduction of gaseous carbon dioxide at the reaction pressure of 30 bar into the calcium acetate solution, a calcium carbonate precipitate is produced at 60 °C. This step also recovers the acetic acid used in step 1:

$$Ca^{2+}{}_{(aq)}+2CH_3COO^{-}{}_{(aq)}+H_2O_{(l)}+CO_{2(g)}\rightarrow CaCO_{3(s)}+2CH_3COOH_{(l)} \quad (12)$$

The inventors argue that the use of acetic acid was selected on the basis that it is stronger than silicic acid but weaker than carbonic acid, which enables the carbonate to displace the acetate during the carbonation step of the process. Using a pulverised wollastonite sample, 48% extraction of calcium was reported in 250 minutes at 60 °C and atmospheric pressure. The extent of carbonation of calcium acetate was considerably less with a maximum of 20% carbonation reported at 30 bar and 60 °C (Kakizawa et al., 2001).

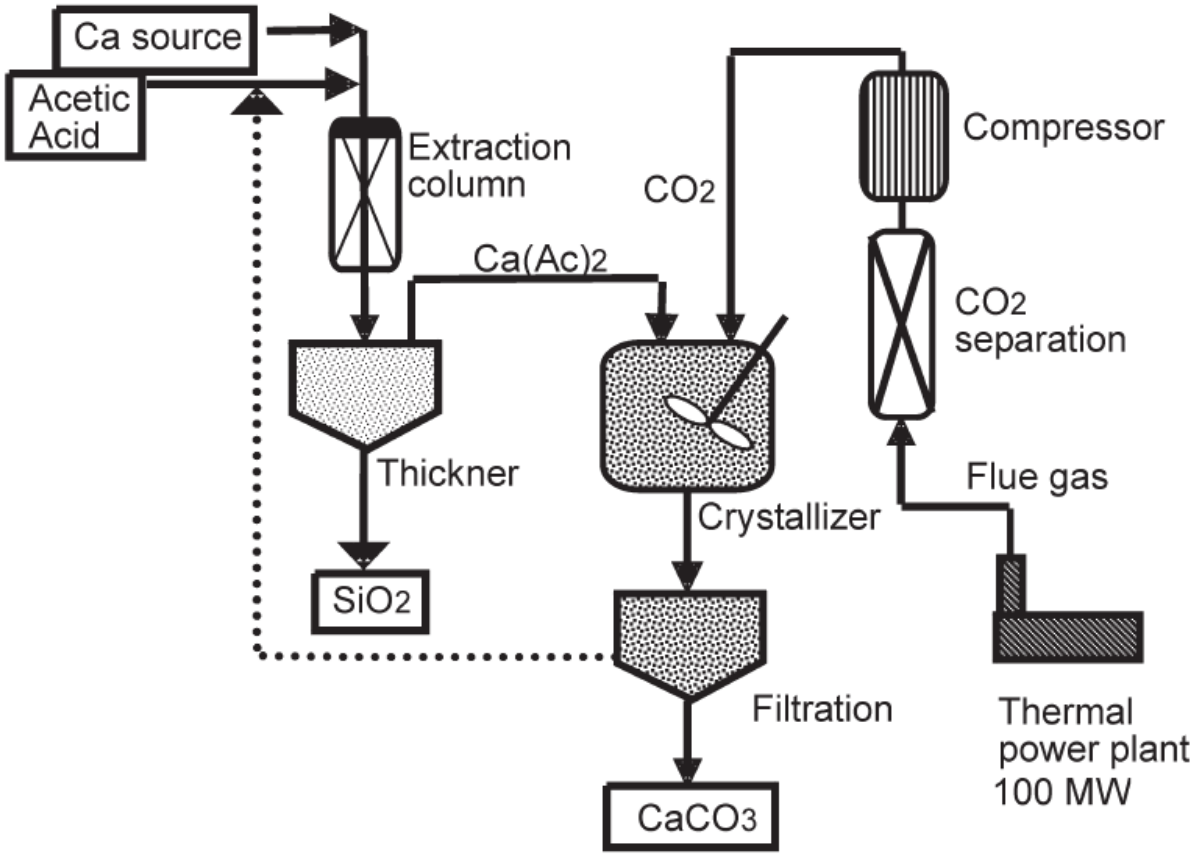


Figure 2-17: Schematic of acetic acid based carbonation of wollastonite (Kakizawa et al., 2001)

The use of this process for the carbonation of more reactive feedstocks such as wollastonite and calcium-rich waste streams such as steel slags (Eloneva et al., 2007) is attractive. It has been suggested that the carbonate product can be used to produce precipitated calcium carbonate (PCC) for the paper industry (Teir et al., 2005). This implies that a product stream of this process can be a useful feedstock to the paper industry, thus eliminating materials handling issues and generating revenues at the same time. Though the use of a less corrosive dissolution presents an attractive process route, the cost-effectiveness of this route is unclear. Furthermore, some researchers have raised concerns as to whether the recycling of acetic acid is feasible without excessive use of energy (Huijgen and Comans, 2003).

Alkali Leach Process

Blencoe et al. (2004) proposed an alkaline-based extraction of the reactive components from the silicate mineral. The process makes use of a concentrated solution of sodium hydroxide to extract (Ca/Mg)-ions at high temperatures and pressure (200 °C, <15 atm) producing reactive hydroxide compounds. Alongside the hydroxide, sodium silicate is produced which the inventors propose can be used to capture carbon dioxide forming sodium carbonate or sodium bicarbonate. These can then be reacted with magnesium hydroxide to produce magnesite and

regenerate the reagent sodium hydroxide (Blencoe et al., 2004). Using olivine as an example, the main reactions for the process are presented:

a. *Alkali Leach*

$$Mg_2SiO_4+2NaOH+H_2O\rightarrow 2Mg(OH)_2+Na_2SiO_3 \quad (17)$$

b. *CO_2 Capture*

$$Na_2SiO_3+2CO_2+H_2O\rightarrow 2NaHCO_3+SiO_2 \quad (18)$$

c. *Carbonation*

$$Mg(OH)_2+NaHCO_3\rightarrow MgCO_3+NaOH+H_2O \quad (19)$$

A number of potential disadvantages for this process have been highlighted (IPCC, 2005; Huijgen, 2007; Wang, 2011). Firstly relatively long reaction times are required (up to 3days) to obtain reasonable recoveries. Secondly, the reaction is reported to require relatively fine particle size (10 microns) which would require extensive grinding. In addition, the ability to recycle the sodium hydroxide solution has yet to be proven. If this is not effective, large quantities of sodium hydroxide required.

2.2 Environmental Assessment

There is a need for the development of technically feasible, carbon-neutral mineral carbonation processes in order to reduce global CO_2 emissions. Though the majority of research and development has focused on the enhancement of extraction and carbonation efficiencies, there is a growing recognition of the need to develop integrated mineral carbonation processes that reduce input requirements in terms of energy and reagents.

A feasibility study conducted by Newall et al. (2000) investigated a number of processes that included the route proposed by Lackner et al. (1995) for magnesium and calcium feedstocks, a direct carbonation approach and an indirect approach that uses a magnesium melt to bypass the use of hydrochloric acid, as is the case in the route proposed by Lackner et al. (1995). A table summarising the processes selected from initial screening of literature by the authors is presented in Table 2-6. Newall et al (2000) narrowed down the selection, through further screening, with the view of selecting one process as "favoured" to be implemented as a sequestration option. To achieve this, "key decision factors" were selected to compare the processes: efficiency of reaction, cost, confidence in process, acceptance and overall applicability.

Table 2-6: Selected carbonation processes from literature (Newall et al., 2000)

Process No.	Raw Material	Raw material reacts with:	CO_2 reacts with:	CO_2 stored as:
1	Mg silicate rock	HCl	$Mg(OH)_2$	$MgCO_3$
2	Mg-rich brine deposit	H_2O	$Mg(OH)_2$	$MgCO_3$
3a	Mg silicate rock	$MgCl_2$	$Mg(OH)_2$	$MgCO_3$
3b	Mg silicate rock	CO_2	$Mg_3Si_2O_5(OH)_4$	$MgCO_3$
4	Ca silicate rock	HCl	Ca(OH)2	$CaCO_3$
5	$MgCO_3$ + NaCl	CO_2	$MgCO_3$ + NaCl	$NaHCO_3$

The study was based on a thermodynamic view of the processes to assess them due to the absence of experimental data on kinetics (Newall et al., 2000). Literature data and approximations of process unit mass and energy requirements were used, as the kinetics of the reactions were not known.

The authors studied two processes in detail: the HCl extraction route proposed by Lackner, as well as the carbonation of the silicate mineral in a melt of $MgCl_2$ (Wendt et al., 1998). These processes were to be developed to sequester 3 million tonnes of CO_2 per year produced by a 500 MWe coal-based power station. Literature data was used to estimate the CO_2 balance of the process, considering quarrying and crushing of the mineral, processing (heating and electricity) as well as waste disposal. The results of this study found that the process proposed by Lackner et al. (1995) resulted in 13.9 Mt/annum CO_2 emissions for the sequestration of 3 Mt/annum carbon dioxide, with the dehydration step accounting for the majority of the emissions. In contrast, the carbonation process using the magnesium chloride melt resulted in only 0.825 Mt/annum CO_2 emissions, amounting to 27% of the carbon dioxide sequestered. However, it should be noted that the carbonation of the silicate mineral in a melt required considerable quantities of make-up magnesium chloride, the impact on the carbon footprint of which was not considered. Considering that the generation of the melt on-site has been estimated to account for a third of annual global HCl production (O'Connor et al., 2005), this may significantly underestimate the potential environmental impact of the magnesium melt approach.

To evaluate the potential of the direct aqueous carbonation process (Section 2.1.2), developed by the National Energy Technology Laboratory - NETL (formerly the Albany Research Center), a study was conducted to establish the energy burdens of this route (O'Connor et al.,

2005) at the optimum mineral specific conditions discussed in Section 2.1.2. The samples used were obtained from seven different regions, with Region 1 and 5 corresponding to olivine, Region 2-4 and Region 6 corresponding to serpentine, and Region 7 to wollastonite. Energy requirements for feedstock preparation and pre-treatment were included in the study, although the energy requirements for reagent production do not appear to have been accounted for. The results are summarised in Table 2-7. This study attributed most of the energy burdens of this approach to pre-treatment techniques such as standard crushing and grinding for all minerals, additional heat treatment of serpentine and mechanical activation through ultrafine grinding of wollastonite and olivine.

Table 2-7: Energy burdens for the NETL mineral carbonation route (O'Connor et al., 2005)

Region	Energy, GW·h (x1000)	CO_2 seq.,Mt[1]	Energy Consumption, GW·h/Mt CO2 seq.			CO_2 avoided, Mt	
			std.[2]	act.[3]	Total	std	act
1	18	18	300	333	633	13	7
2	9	10	180	2022	2202	8	0
3	9	10	180	2251	2431	8	0
4	72	72	180	2022	2202	59	0
5	184	187	320	333	653	126	63
6	220	231	180	829	1009	187	0
7	75	76	190	239	429	62	43

[1] CO_2 sequestered based on coal consumption and carbon content by region, assumes sequestration of 100% of emissions

[2] Energy consumption for complete sequestration operation, including energy for standard pretreatment (crushing and grinding) and carbonation energy

[3] Energy for activated pretreatment, ultrafine grinding (olivine and wollastonite) or thermal (serpentine)

Table 2-7 indicates that for the regions 2-4, as well as region 6 there is zero carbon dioxide avoided due to activation through activation pretreatment. These cases correspond to the use of serpentine as feedstock, which, in addition to crushing and grinding, requires high temperature thermal treatment to improve its reactivity. Significant decreases in carbon dioxide avoided can also be noted for the other regions which correspond to olivine and wollastonite, when ultrafine grinding is used to improve reactivity. These results indicate that serpentine-based direct aqueous carbonation processes are unlikely to be viable for sequestration purposes. Similar findings were presented by Khoo and Tan (2006) who explored carbonation processes in isolation as well as coupled with carbon dioxide capture. However, the study by O'Connor

et al. (2005) appeared to ignore the impact of chemical reagents, which would result in lower carbon dioxide avoided than those reported in Table 2-7, when their impacts were accounted for. Additionally, the study appeared to combine the energy from heat and electricity in their analysis, which may cause difficulty in accounting for carbon dioxide emissions attributed to each energy source.

A gate-to-gate study was conducted to investigate the viability of different routes to sequester carbon dioxide from a 1 GW coal-based power plant, by Kelly et al. (2011). The options considered were the carbonation of brine solutions through the use of industrial caustics such as sodium hydroxide, the direct aqueous carbonation of silicate minerals, as well as the direct aqueous carbonation of industrial wastes such as iron slag and fly ash. The analysis was based on publicly available literature data on these approaches, and rough engineering calculations to estimate energy requirements. Their energy analysis included carbon dioxide capture and major process unit operations such as compressors, mixers and heaters (Kelly et al., 2011). The silicate minerals selected were olivine and wollastonite, the authors arguing these are the most promising feedstocks. The evaluation of process performance was conducted by comparing energy required by the process versus the energy generated by the 1 GW power plant. The use of industrial wastes in brine solutions was reported to result in an energy penalty of 90-100+% of the energy generated. Amongst the silicate minerals, olivine was reported to result in a 55-69%, whereas wollastonite resulted in an energy penalty greater than 100%. The industrial waste, fly ash, reported the least energy penalty (9-22%), whereas iron slag had an energy penalty greater than 100% (Kelly et al., 2011). The separation of carbon dioxide from flue gases and the grinding of the minerals were found to be the energy major burdens, for the olivine, wollastonite and iron slag feedstock, whereas the production of sodium hydroxide was the main contributor to the energy penalty for the brine solutions route. To make the processes feasible Kelly et al. (2011) suggested optimisation of the process to enhance energy efficiency, though opportunities for this were not explicitly identified.

Kirchofer et al. (2012) conducted a life cycle assessment of the direct aqueous carbonation process using different mineral feedstock in order to compare their energy efficiency and carbon dioxide storage potential. The approach the authors took relied upon literature data, patents, assumptions and simple engineering calculations to evaluate mass and energy balances. They used an economic input-output life cycle assessment (EIO-LCA) tool developed at Carnegie Mellon University to convert direct energy consumption to life cycle energy consumption, which includes on-site as well as input requirements. The study by

Kirchofer et al. (2012) considered a variety of mineral carbonation feedstock from natural silicates such as serpentine (Se) and olivine (Ol) to industrial wastes such as steel slags (SS), coal fly ash (FA) and cement kiln dust (CKD). The model used included eight stages across the life cycle of the process from extraction, to chemical conversion to disposal. However, the researchers did not include energy requirements associated with chemical reagent production and the compression of carbon dioxide. Different conditions were investigated with regards to temperature, from 25 °C up to as high as 155 °C. The authors reported that heating and physical pre-processing (crushing and grinding) were major carbon dioxide emissions impacts for the natural silicate minerals as indicated in Figure 2-18.

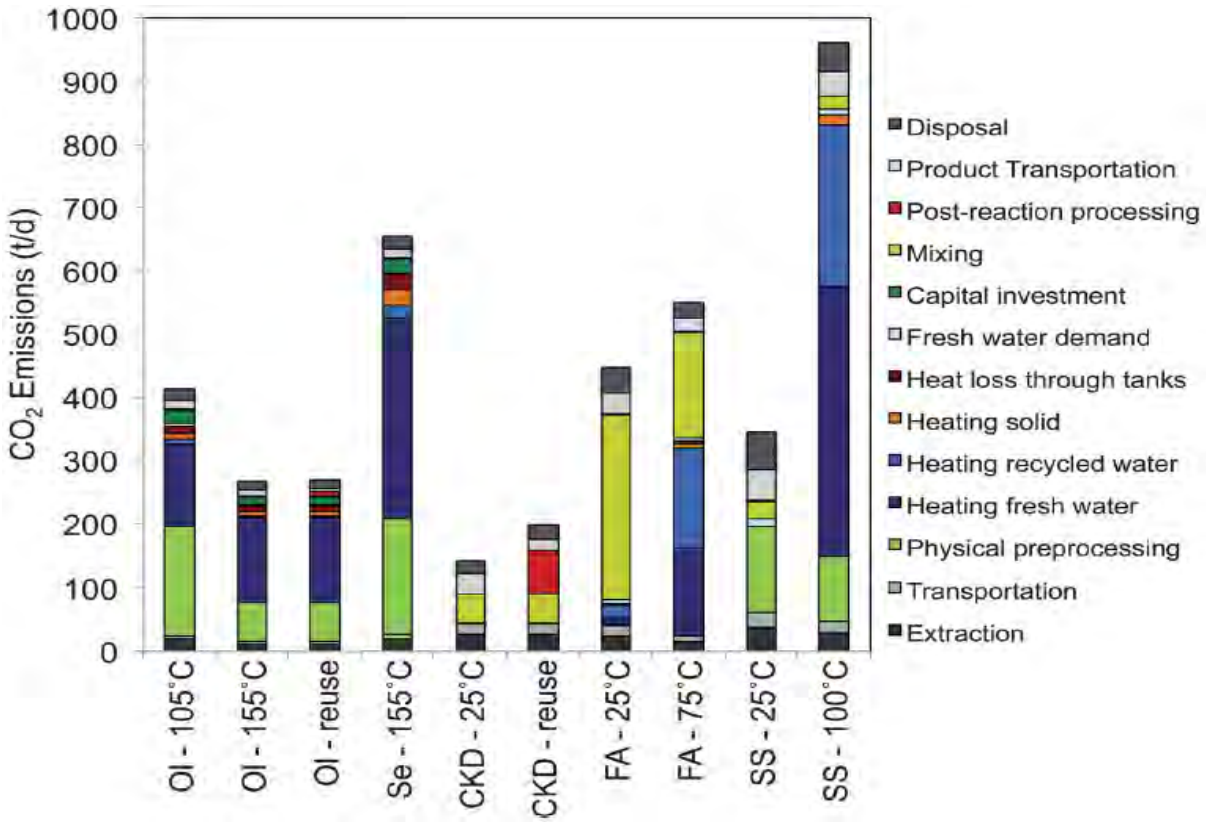


Figure 2-18: CO_2 emissions for the direct aqueous mineral carbonation processes as a function of feedstock and carbonation (Kirchofer et al., 2012)

Regardless, the total carbon dioxide emissions from the processes considered were less than the 1000 ton/day sequestered for all the sources examined. Though this result is encouraging, it is important to note that the model used by the researchers was a general, first-order level model, which could potentially underestimate some contributions. It was duly noted that more detailed process models developed on software like Aspen could provide better estimates for reaction rates and energy requirements (Kirchofer et al., 2012).

The life cycle assessment of the multi-stage process developed by researchers at the Åbo Akademi University (Fagerlund et al., 2009; Zevenhoven et al., 2011) was conducted by another researcher in this group (Ndaugu et al., 2012b). The researchers' work compared the ÅAU process to the direct aqueous carbonation process developed at the NETL. These processes were discussed in detail in Sections 2.1.1 and 2.1.2, respectively. To determine energy requirements, Nduagu et al. (2012b) used literature data for the aqueous carbonation process and developed a simulation on Aspen software for the multi-stage process. The source of carbon dioxide was considered to be a coal-fired power plant based on Canadian/US data from the Ecoinvent database on SimaPro software. The plant was assumed to supply the electricity requirements whereas natural gas was considered for heat supply (Nduagu et al., 2012b). However, the authors did not account for reagent make-up (assuming 100% recovery) for the ammonium sulphate used in the ÅAU process. Additionally, the determination of the amount of reagent ($NaHCO_3$, NaCl) for the NETL process was not based on the material balance (Nduagu et al., 2012b), which underestimates the amounts required and thus the impact in terms of emissions, according to the authors.

The authors used systems expansion through the use of iron and calcium by-products in the iron steel making industry, mass allocation by products, as well as heat integration to reduce environmental burdens of the process by as much as 35% for the multi-stage process. Through the application of an exergy analysis the authors reported significantly lower environmental impacts (683 kg-CO_2e/ton-CO_2) in comparison to 1270-2170 kg-CO_2e/ton-CO_2 when an exergy analysis was not conducted for the NETL process (Nduagu et al., 2012b). The study found that both processes were effective carbon sinks with the multi-stage process having an environmental burden of 517 kg-CO_2e/ton-CO_2 (Nduagu et al., 2012b). This signifies promise for these processes though it must be noted that the impact of potential fresh ammonium sulphate use in the multi-stage process to environmental burdens was not discussed.

A comparison of the CO_2 equivalents sequestered by the NETL direct aqueous carbonation and the ÅAU multi-stage process was also conducted in a more recent study by Giannoulakis et al. (2014). In comparison to the study by Nduagu et al. (2012b), this was a less rigorous evaluation, making use of simple engineering calculations to determine energy requirements. In this case the source of carbon dioxide was either a pulverized hard coal power plant or a natural gas combined cycle (NGCC) power plant in Europe, in the year 2025. The silicate minerals wollastonite, olivine and serpentine were considered for the NETL process and serpentine for the ÅAU process albeit with current achievable conversion (considered to be 75% extraction

and 65% carbonation) as well as improved future conversion (considered to be 80% extraction and 90% carbonation). Three different scenarios are considered for the direct aqueous carbonation process based on feedstock (NETL1 – Wollastonite, NETL2 – Olivine, NETL3 – Serpentine) and two for the ÅAU process, based on extraction/carbonation efficiencies (ÅAU1 – current efficiency, ÅAU2 – future improved efficiency). The authors further compared these processes with geological storage. A summary of their findings with regards to carbon dioxide footprints is presented in Figure 2-19.

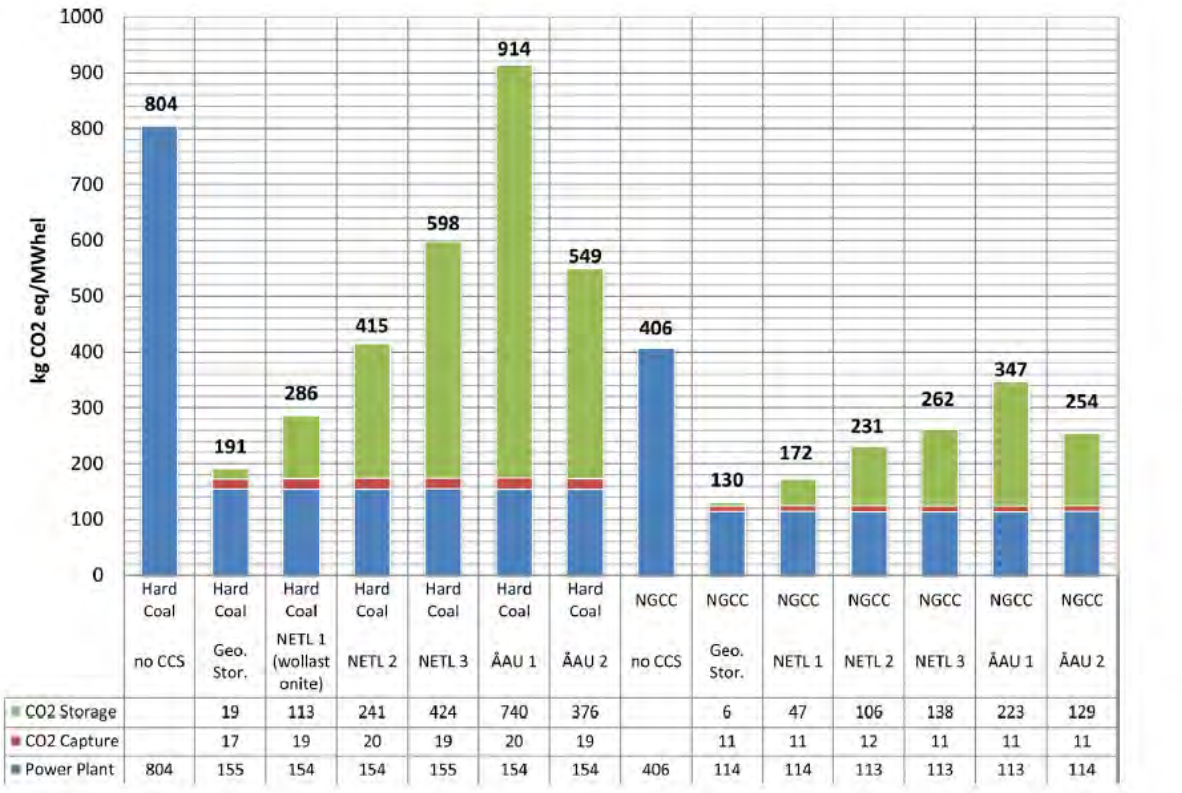


Figure 2-19: Life cycle greenhouse gas emissions for mineral carbonation and geological storage in Europe in 2025 (Giannoulakis et al., 2014)

In most cases, the sequestration of carbon dioxide resulted in a reduction in net emissions from the base case amount of 804 kg-CO_2e. An exception was the ÅAU 1 for hard coal power plant, based on current conversion efficiencies of 75% extraction and 65% carbonation reported by Romao et al. (2012). The major burdens were attributed to solvent make-up, heat and electricity requirements (Giannoulakis et al., 2014). However, for chemical reagent accounting for the NETL process the authors referenced the work by Nduagu et al. (2012b) which underestimates the required input reagents. Additionally, the authors assumed the heat required for the heating of process streams in the NETL process to be balanced by the released by the carbonation reaction, in effect complete heat integration. Although this is a reasonable simplification, the

recovery of the heat from the carbonation reaction may be difficult, as some researchers have noted (Zevenhoven et al. 2011; Olajire, 2013).

2.3 Literature Summary

2.3.1 General Observations

Mineral carbonation has the potential to play a key role in the sequestration of anthropogenic carbon dioxide emissions. The development of this process has spanned more than three decades and has resulted in the development of an array of process routes and processes, all with the objective to permanently store carbon dioxide in stable carbonate compounds. However, considerable challenges stand between the technology and effective sequestration of carbon dioxide, from an environmental and economic stand point.

The direct carbonation of the silicate mineral with carbon dioxide, the simplest approach, and one that offers the most potential for the use of the exothermic energy of the carbonation reaction, has been demonstrated to be prohibitively slow and is thus not suitable for industrial implementation. As a result, the general trends have been towards the development of multi-stage gas/solid carbonation processes or the use of aqueous media to accelerate the process. Current carbonation of silicate minerals in engineered carbonation systems generally requires relatively aggressive, energy-intensive processes and/or pretreatment to enhance the reaction kinetics. Researchers at the Åbo Akademi University (ÅAU) have focused on developing a high temperature multi-stage gas/solid route (Section 2.1.1), whilst the majority of other researchers in this field have been focused on developing aqueous-based carbonation systems (Section 2.1.2 and 2.1.3). In this area, the direct aqueous process developed at the National Energy Technology Laboratory (NETL) has been considered the state-of-the-art. Alternatively, others have pursued indirect aqueous processes such as the multi-stage hydrochloric acid extraction, acetic acid and the alkali leach processes. However, the pH swing method has largely been the most adopted. Several of these have been developed into conceptual flowsheets and some patented, such as the ammonium salts process, with potential to be implemented on an industrial scale due to the reaction times and conversion efficiencies.

Studies on mineral carbonation have mainly focused on the more abundant and reactive silicate minerals wollastonite, serpentine and olivine. Relatively few studies have been conducted using less reactive pyroxene minerals, which are the major source of sequestrable cations in the tailings generated from the processing of PGM ores in South Africa. By extension the processes that have been developed have focused on these minerals, with no known process

having been proposed and evaluated using PGM tailings as a feedstock. The fact that limited research has been done using pyroxene or PGM tailings implies that the understanding of the opportunities that exist in particular process routes is minimal, and that technical operability of the processes beyond the specific mineral is uncertain. This clearly presents a challenge with regards to process selection. Regardless, the selection of process routes can be made, through good engineering judgement, by analysing process thermodynamics and reactivity, keeping in mind the type of feedstock. Review papers give a good indication of the state-of-the-art and thus serve as an additional guide.

Despite the potential advantages of using these tailings as feedstock for a uniquely South African engineered mineral carbonation process, preliminary studies have indicated that relatively aggressive processing conditions and/or long retention times will be required to make this technically feasible. The consequence of using aggressive reaction conditions to accelerate the mineral carbonation process has been the potential to render this approach an ineffective carbon sink, from a net carbon footprint perspective. Recent studies are consistent with an increasing recognition of the need to evaluate the processes using life-cycle approaches to ensure that they result in net CO_2 reduction. However, to date studies have been based largely on rough calculations, simplifying assumptions, and limited use of LCA tools and robust simulation software packages that contain appropriate thermodynamic models to better predict material and energy requirements (Section 2.2). Although the importance of utilising more rigorous mass and energy balance tools such as Aspen Plus has been acknowledged, application has been limited. Additionally, the accounting of carbon dioxide footprints has also been largely conducted on the basis of first-order calculations, rather than by means of a rigorous software framework which takes into account all the relevant processes, including the foreground and background processes. This has led to a lack of consistency and clarity in approach, difficulty in drawing comparisons, and ultimately a compromise of the veracity of the studies.

2.3.2 Summary and Comparison of Mineral Carbonation Processes

The literature review indicated that several process routes exist for the mineral carbonation of silicate minerals. It also demonstrated that within these routes there has been a considerable amount of research that has been done to understand and improve the performance of the processes. Despite this, only a few of these processes have been developed into pilot or commercial projects, with only a direct aqueous based process developed by Shell having been demonstrated on a pilot scale, whereas the brine solutions based SkyMine process (by a joint

venture that includes BP and Conoco-Phillips) has been commercially implemented to sequester 83 000 tCO_2 per annum (Sanna et al., 2014b).

The direct gas-solid carbonation route has been developed from the simple single-step process to a more complex multi-step indirect process. This indirect route has achieved notably higher conversions and better reactivity through the use of magnesium hydroxide as the carbonation feedstock. The ÅAU process, which uses ammonium sulphate to extract magnesium from serpentine, and subsequently producing magnesium hydroxide to be carbonated, offers promising levels of extraction. Typical extraction efficiencies have been reported to be around 64-66% whereas carbonation efficiencies have been reported to reach a maximum of 55% (Nduagu et al, 2012a; Nduagu, 2012). Some have even set future targets of conversion up to as high as 90% (Romao et al, 2012). However, this process uses energy intensive conditions for the extraction stage, with temperatures as high as 400 °C. The researchers have claimed that their approach allows for the recovery of energy released by the carbonation reaction (Zevenhoven et al., 2011; Nduagu et al., 2012b), which occurs at around 450 °C and 20 bar. A literature review on life-cycle assessment studies of this process has provided conflicting findings with one study suggesting that process could result in a net release of carbon dioxide (Giannoulakis et al., 2014) whereas another conducted by researchers at the ÅAU suggested the process could result in net sequestration of carbon dioxide through the use of mass allocation, systems expansion and energy integration (Nduagu et al., 2012b). These were not considered in the study by Giannoulakis et al. (2014), who used simpler first-order approximations of energy and carbon footprints. Despite the use of high temperature and pressure conditions, this process is promising due to the recycling and possible energy integration opportunities. The application of this process to silicate mineral feedstock other than serpentine has not been discussed in the literature.

The direct aqueous mineral carbonation process, developed at the NETL, has been reported to provide relatively high conversion for the major silicate minerals (Gerdemann et al., 2007), and can also be considered a simpler carbonation processes. The development of this process has evolved from the use of distilled water, to the addition of chemical reagents like sodium chloride and sodium bicarbonate. Laboratory testwork conducted on serpentine, olivine and wollastonite indicate that the optimum conditions vary according to the silicate mineral, but generally require high pressure (>40 atm P_{CO_2}) and temperature (>100 °C). The overall carbonation efficiency of these minerals has been reported to be more than 50% for the least reactive mineral, serpentine, and up to 80% for the most reactive mineral, olivine, under the

optimum conditions (O'Connor et al., 2005; Gerdemann et al., 2007). The pre-requisite high temperature pretreatment of serpentine and grinding of the silicate mineral to particle sizes below 75 microns results in prohibitively high energy requirements (O'Connor et al., 2005). Hence, avoiding the need for heat treatment appears to be key to the viability of serpentine as a feedstock and might justify the use of chemical activation, through reagent use, to extract the alkaline metals as an alternative (Park and Fan, 2004; Teir et al., 2007a). The process has also been evaluated from a life cycle assessment perspective (Nduagu et al., 2012b; Giannoulakis et al. 2014). Both studies have indicated that the direct aqueous carbonation process results in net sequestration of carbon dioxide for wollastonite, olivine and serpentine. However the authors appear to not have adequately accounted for chemical reagent make-up and assuming recoverability of carbonation heat of reaction. This is unlikely to be achievable in practise. Nevertheless, the preliminary results are promising and the simplicity of the process makes it attractive.

Indirect aqueous processes have been noted to offer opportunities for individual optimisation of process steps. These processes involve a series of at least two process steps prior to carbonation of the metal ions extracted from the silicate mineral matrix. Several indirect aqueous mineral carbonation processes have been discussed in this review. Of the indirect aqueous mineral carbonation processes, the pH swing process has been the subject of the most research (Park et al., 2003; Park and Fan, 2004; Teir et al., 2007a; Wang and Maroto-Valer, 2013; Meyer et al., 2014). The review has shown that various acidic chemical reagents can be used for extraction, including inorganic acids, organic acids, ammonium salts or even a mixture of these. The adjustment of the pH can be achieved through the use of various basic reagents such as sodium hydroxide and ammonium hydroxide. The ammonium salts process (Wang and Maroto-Valer, 2013), developed mainly for serpentine feedstocks, shows great promise through its integration of capture, regeneration and sequestration. This is a conceptual process, based on a process developed by Pundsack (1967), which has been patented in the United States by the authors (Wang and Maroto-Valer, 2013). The operating conditions have been reported to be 90 °C for extraction and 80 °C for carbonation. The researchers have reported extraction efficiencies of more than 60% and carbonation efficiencies of more than 90%, for serpentine samples. On the other hand, using the same extraction reagent (ammonium bisulphate), Sanna et al. (2014a) has reported extraction efficiencies of 30% for magnesium from pyroxene, a major component of PGM tailings. Despite the apparent advantages of the ammonium salts process, no detailed energy analysis and carbon footprint evaluation has been conducted to

date. The high temperature used for evaporation of water prior to the high temperature thermal decomposition of ammonium sulphate is concerning, as highlighted by Dri et al. (2014).

As an alternative to this process, based on dissolution and carbonation studies conducted on pyroxene and PGM tailings (Vogeli et al., 2011; Meyer et al., 2014), a hydrochloric acid based pH swing method has been reported to attain extraction efficiencies of 20% and carbonation efficiencies up to 69% (Vogeli, 2012). This approach is the only reported route to have been used to conduct carbonation experiments with PGM tailings as a feedstock. It is worth noting that studies have been limited to preliminary laboratory scale tests, with no testwork on the recovery and regeneration of reagents. Similarly, no assessment of the carbon dioxide balance has been conducted.

Lackner's multi-stage hydrochloric acid extraction process, developed on the basis of serpentine (Lackner et al., 1995), is another example of indirect aqueous processes. This is a conceptual process developed without accompanying experimental data by the researchers. This process converts cations in the silicate mineral into more reactive magnesium hydroxide, and subsequent conversion of the more reactive hydroxide to carbonate. The potential to recycle hydrochloric acid during dehydration of magnesium chloride could reduce material requirements of fresh hydrochloric acid feed. Though this is an attractive element of this process, some authors have pointed out that this regeneration comes at the expense of substantial amounts of energy that threaten process sustainability (Newall et al, 2000). Another multi-stage, indirect aqueous process, the acetic acid process, has been shown to be only viable for reactive feedstocks such as wollastonite and industrial wastes (Kakizawa et al., 2001). The alkali leach process (Blencoe et al., 2004), which involves the use of sodium hydroxide as the leaching agent, has been reported to require long reaction times of up to 72 hours for the extraction stage, ultrafine grinding (<10 μm) of the mineral, as well as potentially large quantities of reagent input due to unproven sodium hydroxide recycle (IPCC, 2005; Huijgen, 2007). Table 2-8 summarises the key attributes of selected mineral carbonation processes.

Table 2-8: Summary of selected processes and their key attributes

Selected Processes	Mineral Tested	Chemical Reagents	Temperature	Pressure	Conversion	References
Ammonium Salts (Indirect pH Swing)	75-150 µm Serpentine	1.4M NH_4HSO_4	90 °C - extraction 80 °C - carbonation	atmospheric	>60% extraction >90% carbonation	Wang and Maroto-Valer, 2013; Wang, 2013
Lackner's Multi-stage (Indirect Multi-stage)	Serpentine	HCl	80 °C – extraction 407 °C - carbonation	atmospheric	N/A	Lackner et al., 1995; Newall et al., 2000
Åbo Akademi University (Indirect Multi-stage)	75-125 µm Serpentine	$(NH_4)_2SO_4$	400-440 °C – extraction 450-500 °C - carbonation	atmospheric – extraction 20 bar - carbonation	64-66% - extraction 50-55% - carbonation	Fagerlund et al., 2010; Nduagu et al., 2012 a/b; Nduagu, 2012
Mineral Acid pH Swing (Indirect pH Swing)	75-106 µm PGM tailings	2M HCl 15M NaOH	70 °C - extraction 20 °C - carbonation	atmospheric	5-20% extraction 48-69% carbonation	Vogeli, 2012; Vogeli et al., 2011; Meyer, 2014; Meyer et al., 2014
National Energy Technology Laboratory – NETL (Direct Aqueous)	75 µm heat-treated serpentine	0.64M $NaHCO_3$ 1M NaCl	155 °C	115 atm	>50% conversion	O'Connor et al., 2002; Gerdemann et al., 2007
	75 µm Olivine	0.64M $NaHCO_3$ 1M NaCl	185 °C	150 atm	80% conversion	
	75 µm Wollastonite	Distilled Water	100 °C	40 atm`	>70% conversion	

Chapter 3

Methodology

Based on the literature review and analysis, a number of mineral carbonation processes have been identified for further assessment, in terms of their carbon balance. The selection of the processes was generally made on the basis of attempting to cover several process routes, identifying promising processes within those routes keeping in mind the relatively inert nature of pyroxene considered as feedstock, reaction times as well as recycle and regeneration opportunities. This meets the first objective of the dissertation: "*Identify potentially feasible flowsheets for the mineral carbonation of PGM tailings on the basis of literature data and information.*" The selected processes include:

i. The Ammonium Salts Process – Indirect Aqueous pH Swing
ii. Lackner's HCl Multi-stage Process – Indirect Aqueous
iii. The ÅAU Process – Indirect Multi-stage Gas/Solid
iv. Mineral Acid pH Swing Process – Indirect Aqueous pH Swing
v. The NETL Process – Direct Aqueous

This chapter outlines the methodology applied to address the second and third objectives of the dissertation:

II. Develop mass and energy balances for the identified processes using process simulation software.
III. Establish the carbon footprint of the selected mineral carbonation processes using a life-cycle based approach.

The development of potentially feasible mineral carbonation process flowsheets involves the use of block flow diagrams, developed into flowsheets, that cover the mass and energy balances of the mineral carbonation process (foreground), as well as the mass and energy balances of process inputs (background). The flowsheets developed are based on data and information reported in available literature (including journal papers, patents, public reports, dissertations and conference proceedings), supported by engineering heuristics and in-house knowledge.

These diagrams form the basis for the development of Aspen Plus™ v8.0 simulations that are used to compute the mass and energy balance of the mineral carbonation processes. The mass

and energy balances obtained from Aspen provide process material and energy requirements that are used for background process modelling to evaluate the overall emissions burden of the selected mineral carbonation process. This is conducted through accounting for the CO_2 footprint of the heat and electricity requirements of the process, production of process reagents including water, and the compression of CO_2 for transportation and process use. The life-cycle impact assessment (LCIA) software SimaPro v7.3.3 is used to conduct this accounting through converting material and energy requirements to CO_2 emission equivalents that result from these processes and operations, giving rise to the total CO_2 burden for the mineral carbonation process.

This value is then compared to the CO_2 that the process sequesters to give an indication of the net carbon footprint of the process. This approach is summarized in the schematic shown on Figure 3-1. Subsequent sub-sections of this chapter provide further information on the goal and scope of the study, and the modelling of mass and energy balances, as well as CO_2 emissions accounting. Detailed descriptions of the goal and scope of the study, the mass and energy balance modelling and carbon dioxide emissions accounting are provided in Sections 3.1, 3.2 and 3.3, respectively.

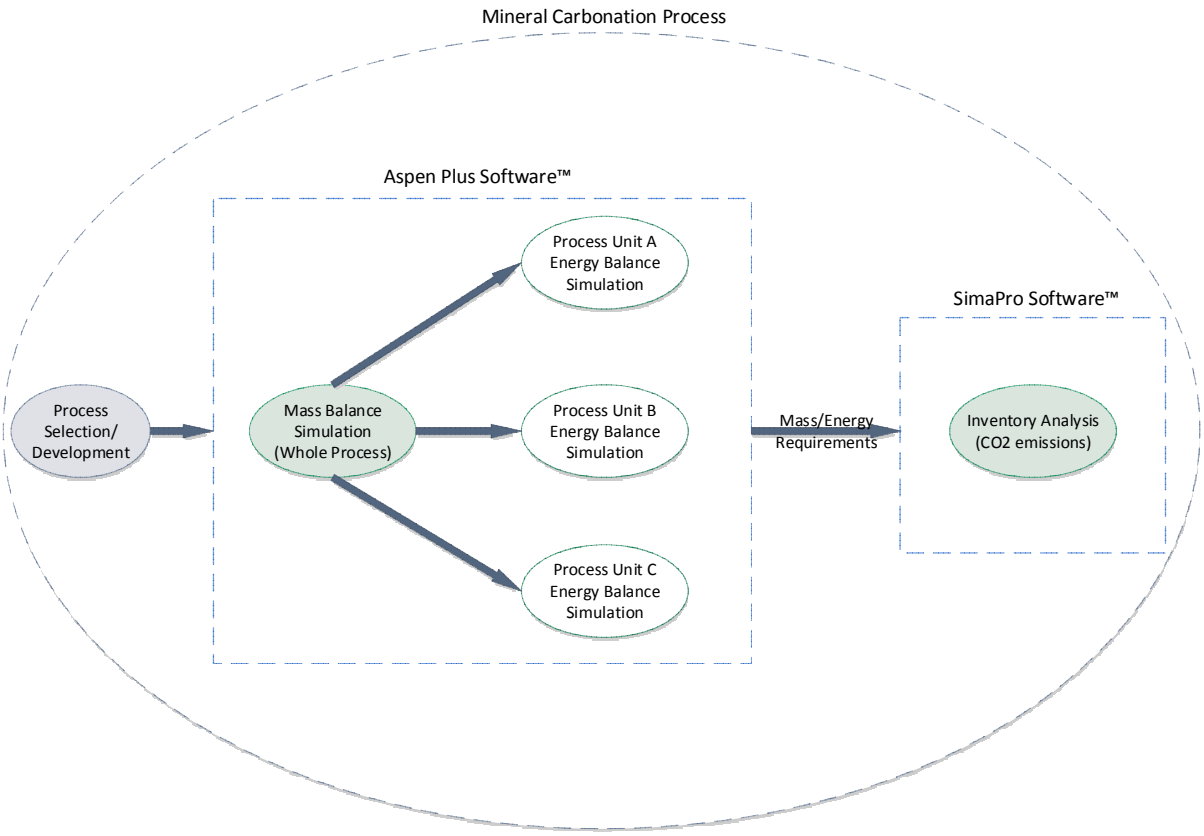


Figure 3-1: Research approach summary

3.1 Goal, Scope and Limitations

According to ISO (2006) the goal of a study should include the reasons to carry out the study, the intended application as well as the intended audience. This is also the place where system boundaries for the study are defined and the functional unit stated (Finnveden et al., 2009). The goal of this study is to evaluate selected processes for mineral carbonation in terms of their effectiveness to sequester carbon dioxide, using PGM tailings as the silicate mineral feedstock. This enables the identification of sustainable processes that can be implemented, as well as identify areas that are burdensome to the process. This will aid researchers in focusing research efforts on promising routes, eliminate unsustainable processes, and provide viable options for decision makers interested in implementing these processes in South Africa.

Streamlining, boundaries and assumptions are crucial (Khoo, 2007) since it is impossible to include every single facet of the processes' life cycle stages. The system boundary used in this study could be classed as that "between the technical system and the environment", using classifications defined by Guinée et al. (2002). Figure 3-2 shows the system boundary defined for the evaluation of the mineral carbonation process routes. This indicates the key inputs to the process, and demonstrates that this boundary is consistent with a cradle-to-gate approach.

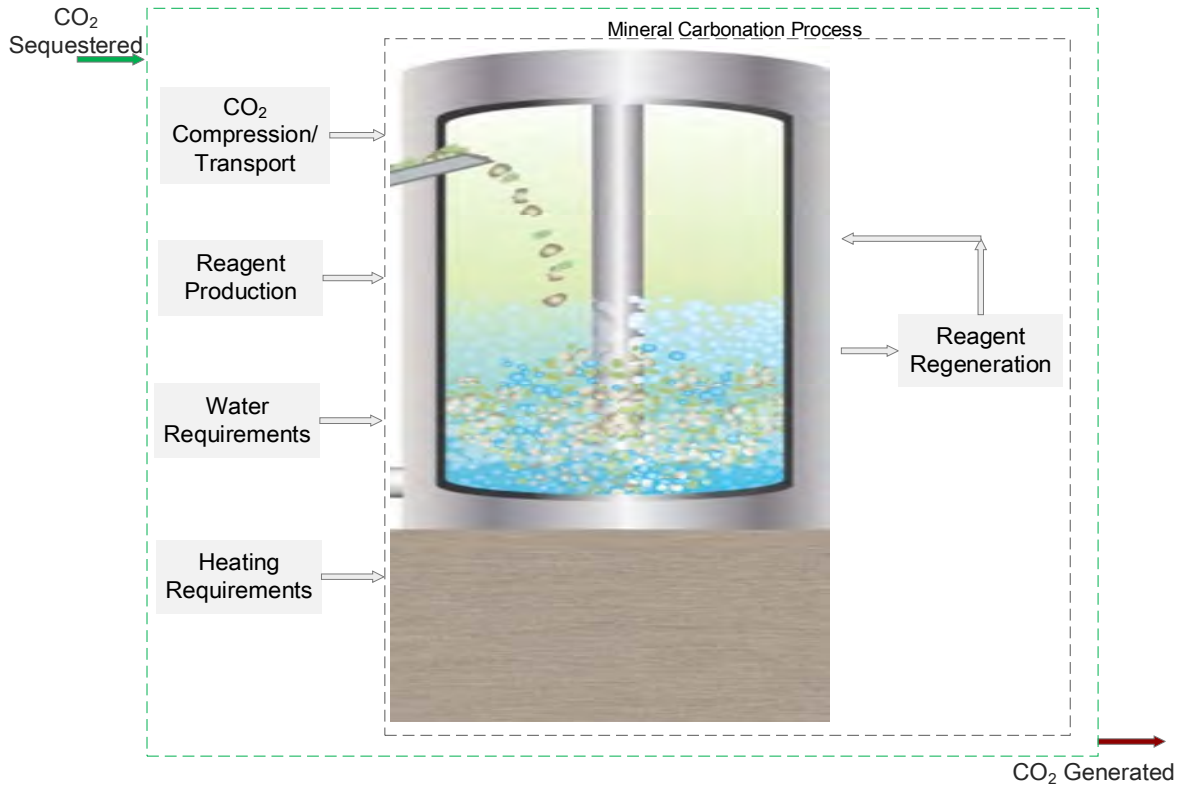


Figure 3-2: System boundary of mineral carbonation processes

This boundary covers impacts from background processes such as generation of heat through the combustion of methane, electricity for the compression of carbon dioxide for transport and plant use, water and chemical reagents required. Regeneration of reagents and its impact are also taken into consideration. The system boundary ends at the point in which the mineral carbonation products are formed, and does not take into account downstream processing or utilization of these products. The transportation of PGM tailings is not considered since it is assumed that the mineral carbonation plant will be located close to the tailings dumps. The effect of mining and processing of the silicate mineral (PGM tailings) used is not considered since this stream is obtained as a waste stream from platinum production and is common to all the mineral carbonation process. It is assumed that this material is considered to be suitable for processing as is, and that no further grinding and/or dewatering will be required. The disposal and treatment of waste is not considered because the carbonate compounds are stable, and the land used to collect the tailings could be used to store the carbonation products. Furthermore, the impact of materials of construction of the mineral carbonation plant have not been considered.

The functional unit is a quantitative description of the performance of the product system or systems (Rebitzer et al., 2004). It describes the primary function fulfilled by the product system (Guinée et al., 2002). This allows for systems or processes to be treated as functionally equivalent and thus comparable, which enables selection of promising processes. Considering that the primary function of the mineral carbonation process is the sequestration of carbon dioxide, the functional unit of 1000 kg of carbon dioxide sequestered was selected. As a consequence of this the impact category selected was the climate change category.

The primary limitation to the data used in this study is that, as has been discussed in Section 3.1, the majority of the proposed processes have been based on wollastonite, olivine and serpentine. The primary component of the PGM tailings feedstock is pyroxene (Vogeli et al., 2011; Meyer et al., 2014). This presents challenges with regards to the chemical reactions and conversions that could be attained with PGM tailings as a feedstock. The first challenge has been overcome by making the assumption that pyroxene will react to produce similar products to olivine, since they are chemically similar. To overcome the second challenge, it was noted that pyroxene is less reactive in comparison to the other silicate minerals (Meyer, 2014). This required conservative estimates of conversion to be assumed, in line with this observation.

3.2 Mass and Energy Balance Modelling

The evaluation of material and energy balances is conducted using Aspen Plus software v8.0. Aspen Plus™ is a robust chemical process simulation software that allows for process model development and simulation. This includes the ability to specify components, thermodynamic models, process units as well as operating conditions. As a result, this enables the prediction of process behaviour, the opportunity to run different scenarios and conduct "what if" analyses, performing sensitivity analyses, as well as allowing for process optimisation (Aspen Plus Manual, v8). A general approach is taken to the development of mass and energy balance simulations, though each particular process has specific details involved with them. A summary of general assumptions is initially discussed.

3.2.1 General Assumptions and Approach for Model Development

The recommended approach in developing simulations on Aspen is to do so in a block-by-block manner, that is, building the simulation gradually and running it every time a new unit is built into the model. Sinnot and Towler (2008) refer to this approach as to "creep up on" the solution. This makes it easier to troubleshoot and find sources of errors in the model, because if errors arise after a particular change to a working simulation, then the source of errors is associated with that change. This is particularly crucial in complex simulations that involve numerous process units and recycle streams, which may be vulnerable to convergence problems.

To take it a step further, the simulations are further broken down into separate mass and energy balance simulations. The mass balance for the whole process is conducted separately, and then energy balances based on that mass balance are conducted for individual process units or smaller groups of units. The benefit of this approach is that it makes identifying bugs in the simulations easier whilst also reducing computation time for the simulations.

The basis for the material balance was 1 ton/hr of carbon dioxide fed into the process. This process flow rate was selected a result of the functional unit, and for the ability to compare results to other processes and studies on the basis of emissions released per ton sequestered. Assuming perfect scale-up, the flows can then be adjusted to satisfy a future supply-specific (e.g. annual output of CO_2 from Sasol, Secunda) process design should the process demonstrate sustainability on the basis of a unit CO_2 sequestered. The mineral feedstock to the proposed mineral carbonation process will be PGM tailings sourced from mining operations of companies like BRPM, Impala, Northam and Lonmin. This feedstock is available as fine-

milled particles (<150 μm) according to Vogeli et al. (2011), thus it is assumed it will require no further grinding or milling, as discussed earlier. The major component (~65wt%) in PGM tailings is pyroxene (Vogeli, 2011; Meyer, 2014). For the sake of simplicity, the feed material is thus assumed to be pyroxene (enstatite) in all process systems studied here.

The impact of the transport of mineral feedstock was assumed to be negligible since the mineral carbonation plant would be located close to this feedstock. The pumping of materials, separations and mixing impacts were not included in energy calculations as these were assumed to be much smaller than heating and compression. Separations of phases and components were assumed to perfect for simplicity, with the recognition that this wouldn't be the case in practice. The selection of the type of separation process depends on the differences in the physical or chemical properties of the components. The effectiveness of the separation between phases/components depends on the exploitation of differences in molecular, thermodynamic and transport properties (Seader and Henley, 2006). Since this is a preliminary study of these processes, the level of detail required in this analysis was considered to be outside the scope of this study. The compression took into account the compression for transport by pipeline as well as any additional compression required to raise the pressure from the pipeline pressure for process purposes. In the case where processes operations occurred at lower pressures than the pipeline pressure, a turbine was used to reduce pressure thus generating an electricity credit.

Due to the absence of processes based on pyroxene, the processes are assumed to exhibit similar chemistry to these minerals, with regards to how they react (as suggested in literature/patent), though the conversions (single pass) are adjusted according to those obtained in literature for pyroxene, as has been discussed in Section 3.1. In the absence of experimental data, conservative estimates of these single pass conversions are made, particularly for the leaching step. Conversions of other processes excluding carbonation and dissolution are assumed to 100%. Process specific assumptions are outlined in the relevant sub-sections of the Chapter 4.

3.2.2 Property Methods Selection

A property method is a collection of routes for the calculation of properties needed by unit operation models. The selection of the appropriate method for estimating thermodynamic properties of pure components and mixtures is one of the most important steps in the development of a simulation. This decision affects the entire simulation, and the results that will be produced when the simulation is conducted. To ensure meaningful results are obtained

from simulations, it is vital to ascertain that the property method selected is representative of the system being modelled.

Aqueous Operations

The Aspen Physical Property System manual recommends electrolyte activity coefficients models for mineral leaching and hydrometallurgical operations (AspenTech, 2013). The most versatile of these models is the ELECNRTL property method. Due to the presence of electrolytes in these processes, the thermodynamic model selected to model aqueous systems in the selected carbonation processes was the ELECNRTL property method. This property method can handle electrolyte systems with very low and high concentrations. This is achieved through binary parameters that model the interactions of true species in aqueous single electrolyte systems, and multicomponent systems. Another strength of this model is that it is effective across a wide range of temperatures (AspenTech, 2013). In this model, the liquid phase and heats of mixing are modelled through the electrolyte NRTL model, whereas the vapour phase properties are modelled through the Redlich-Kwong equation of state. A number of unit operations across the mineral carbonation process routes are of aqueous nature. This means that a majority of the process units will be modelled using this property method, with the exception of specific operations like the compression of CO_2 and the gas-solid reactions in the ÅAU process. The property method selected for each unit operation will be presented in the table for input specifications in Appendix A:.

Gaseous and Gas-Solid Operations

Though most processes in the proposed mineral carbonation routes are of an aqueous nature, some unit processes within these routes cannot be classified as such. This means that the property method used for these processes needs to be appropriate to the unit it attempts to describe. Carbon dioxide that needs to be sequestered by the process has to be compressed in order to be transported by pipeline to the carbonation site, and for use in unit operations of some of the mineral carbonation processes. To model the compression of the gas, the RK-SOAVE property method was selected. The Redlich-Kwong-Soave (RKS) equation of state model is appropriate for gas processing of hydrocarbons and light gases, such as carbon dioxide, hydrogen sulphide and hydrogen (AspenTech, 2013). The carbonation reaction in some process routes (HCl extraction, AAU process) involves a gas-solid reaction between carbon dioxide and magnesium hydroxide. The extraction process in the ÅAU process can also be classified as a gas-solid process, since ammonium sulphate decomposes into gas phase at the reaction temperature. The UNIQUAC property method was selected to model these process

units. This model is an activity coefficient model that is capable of handling any combination of polar and non-polar compounds, up to very strong non-ideality (AspenTech, 2013).

3.2.3 Simulation Development Illustrations

The development of simulations for processes is based on process routes proposed in literature. The flowsheets of these processes are developed and built up on the Aspen Plus simulation package. The resulting simulation diagrams are presented in Appendix E for each mineral carbonation process considered.

The chemical components that are involved in the particular process are selected and input into the "Components" tab as indicated in Figure 3-3. The components added into this tab are not just reagents but also include products of process units as well as the mineral carbonation process in general.

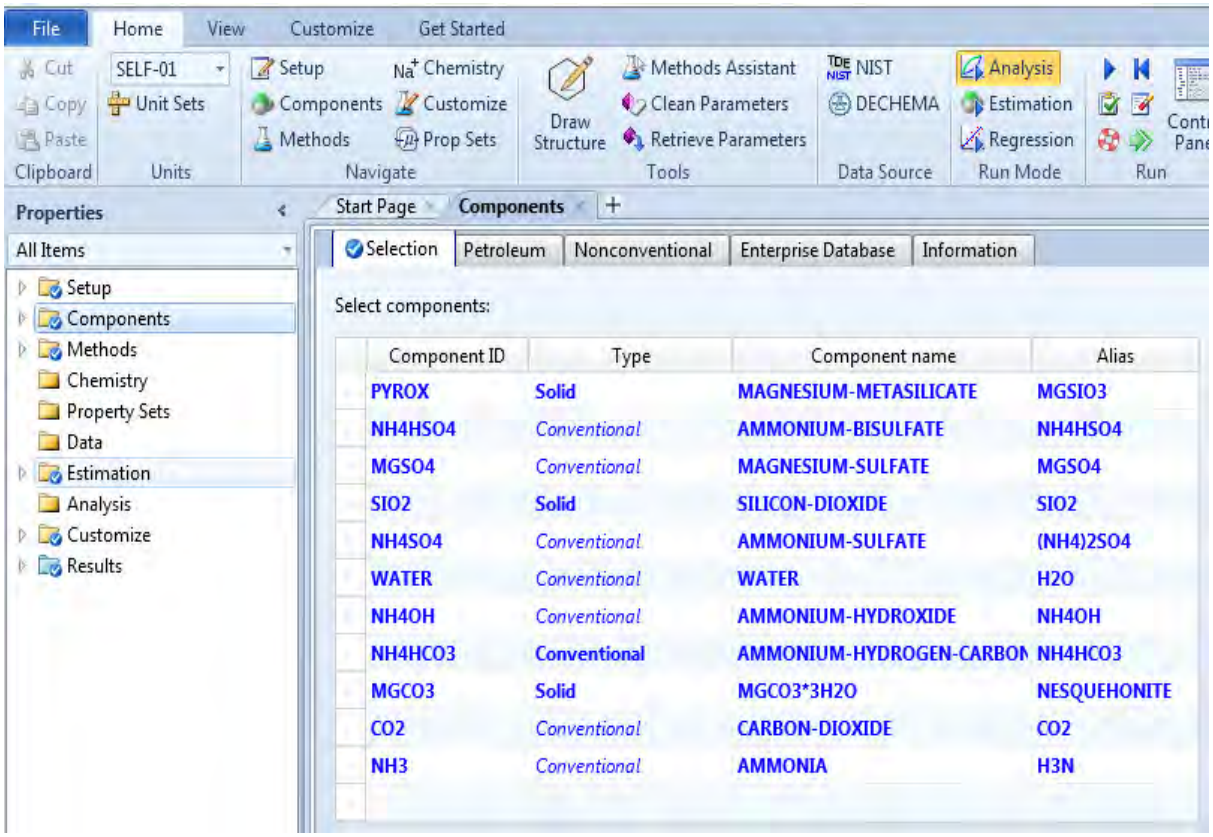


Figure 3-3: Chemical component input on Aspen Plus simulation software

The next step is the definition of the property method used in the process shown in Figure 3-4. As discussed in Section 3.2.2, the property method used for aqueous processes was the ELECNRTL property method, and for gas and gas-solid operations the RK-SOAVE and UNIQUAC property methods can be used. These can be selected by navigating to the "Methods" tab and browsing through the list of property methods on Aspen until the

appropriate method is found. These two steps fall in the "Properties" tab of the simulation interface, and clicking next will run the properties package, as configured by the user, in preparation for the simulation. The next step is to navigate to the simulation environment by moving to the "Simulation" tab. Here, the simulation diagrams presented in Appendix E are developed. Each process unit block and process stream has to be initialized with input data in order to complete the simulation. The input data for initializing all the simulations is presented in Appendix A.

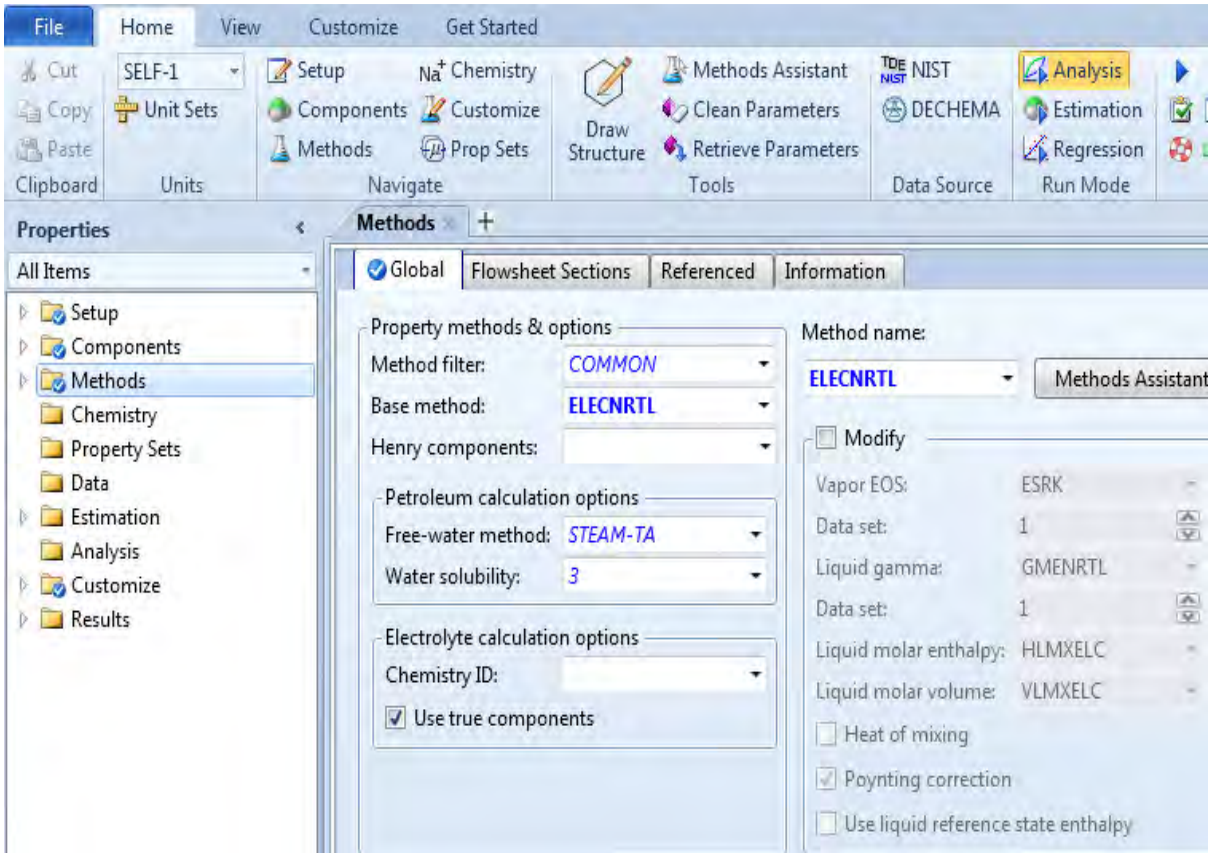


Figure 3-4: Property method selection Tab on Aspen Plus simulation package

3.3 Carbon Dioxide Emissions Accounting

The material and energy requirements of the mineral carbonation process serve as the basis for the calculation of carbon dioxide footprint that will result from the implementation of the selected process. These include emissions associated with the production of chemical reagents, supply of water, generation of process heat, and supply of electricity for the compression of carbon dioxide. To determine these contributions the sources and processes used to generate these requirements need to be determined, in order to use background process modelling software to establish the emissions associated with the requirements. The first sub-section (3.3.1) of this section will deal with establishing sources and processes for generating process

requirements, whereas the second subsection (3.3.2) will discuss the approach taken to calculate resulting emissions.

3.3.1 Inventory Analysis

The discussion of input materials into the mineral carbonation process has been separated into two parts; the discussion of those inputs that are common in all processes, and the discussion of those that are specific to certain processes.

Common Process Inputs

Carbon Dioxide

The CO_2 stream feeding into the mineral carbonation process is assumed to be a pure stream of CO_2, since the SASOL synfuels process produces a high purity CO_2 stream (Cloete, 2006; Vogeli et al., 2011). All carbonation processes are developed on the basis of 1 ton/hr of CO_2 sequestered. Since the synfuels plant and the mine tailings site are not located on the same site, in fact about 300 km apart, transport of materials is necessary. According to Giannoulakis et al. (2014) it is more preferable to transport CO_2 to the mine site than transporting the large quantities of rock to the emissions site. This implies that options for the transport of CO_2 need to be considered.

The transport of CO_2 can be carried out through tanks, ships or pipelines. The selection of the method of transport is dependent on the volume being transported and the distance (IPCC, 2005; Leung et al., 2014). The most preferable method for transporting carbon dioxide through long distances on land is by the use of pipelines (Svensson et al., 2004; Koornneef et al., 2010). This is because motor carriers and railways are expensive and lack capacity (Svensson et al., 2004). Transportation of CO_2 by pipelines is not new (IPCC, 2005) with a network of 2500 km in the United States having been implemented for the purposes of enhanced oil recovery (EOR). In South Africa, Sasol currently operates a natural gas pipeline from the Temane and Pande gas fields in Mozambique (PWC, 2012). The knowledge from operating natural gas and hydrocarbon pipelines can be used for implementation of CO_2 pipelines (Svennson et al., 2004), since transportation conditions are similar.

Transportation of CO_2 at low pressures is possible, but due to low density of the fluid in these conditions, the capacity required to transport meaningful amounts of CO_2 would be substantial. The more preferable option is to transport it in supercritical state, where it has a high density as liquids but viscosity similar to that of gases (Wildbolz, 2007; Leung et al., 2014). The recommended conditions for the transportation of carbon dioxide are between 13 °C and 44 °C

and pressures above the critical point (73.9 bar and 31.1 °C), typically between 85 atm and 149.6 atm (WRI, 2008, Leung et al., 2014). This pressure can then be throttled up or down depending on process requirements using either a compressor or turbine respectively, as discussed earlier. Literature suggests recompression is necessary every 150km, but practice has shown transport without recompression for distances above 400 km (Wildbolz, 2007). Since the transport distance is 300 km (less than the 400 km), it is assumed that recompression will not be necessary.

Heat, Electricity and Water

A number of unit operations in the mineral carbonation process require heat to be supplied to them. Industrial operations typically use fossil fuels (coal, natural gas, oil) and biomass (bagasse, vegetable oil, wood chips) to generate heat (Thekdi, 2007). Gaseous fuels such as natural gas are commonly preferred for use in industrial heating since they burn cleanly and completely without producing soot particles (Baukal, 2000; Liang et al., 2012). Natural gas is also less costly per unit of energy (Liang et al., 2012) in comparison to oil and coal. The natural gas pipeline from Mozambique carries 240 million gigajoules per annum of which about half is used by Sasol in the GTL process, with the balance being available for commercial and industrial customers (PWC, 2012). For the purposes of providing heat, for all selected mineral carbonation process routes, natural gas was selected as the supply due to the reasons outlined. Some other unit operations in the mineral carbonation process, such as compression, require electricity. The proposed mineral carbonation plant will be located in South Africa, and the electricity mix selected consistent with the South African scenario. For all cases where water was required, process water from surface water was assumed as the source.

Process Specific Inputs

Ammonium Bisulphate

The ammonium salts based pH swing process proposed by Wang and Maroto-Valer (2011) makes use of ammonium bisulphate for the extraction of cations from the silicate mineral. This compound is formed when ammonium sulphate salt is heated in an open system to temperatures above 100 °C, which causes it to decompose into ammonium bisulphate and ammonia (Kirk-Othmer, 2007). The authors of the ammonium salts mineral carbonation process patent also suggest the use of this mechanism to regenerate ammonium bisulphate (Wang and Maroto-Valer, 2013). The production of ammonium bisulphate for use in the mineral carbonation process will be assumed to be from the use of ammonium sulphate as a feedstock.

Ammonium Sulphate

This chemical compound is used to extract the magnesium from the silicate mineral through the process proposed at Åbo Akademi Univesity (Fagerlund et al., 2012; Nduagu, 2012). According to Kirk-Othmer (2007), ammonium sulphate is produced through direct neutralisation of aqueous sulphuric acid with gaseous ammonia. This process will be assumed to be the means of production of ammonium sulphate for use in the Åbo Akademi process.

Ammonium Hydroxide

Ammonium hydroxide, which is a solution of ammonia in water, is used to adjust the pH in the ammonium salts process (Wang and Maroto-Valer, 2011). The production of ammonia occurs through the reaction of nitrogen gas with hydrogen gas, in a fairly simple reaction originally developed by Fritz Haber and Carl Bosch (Appl, 2005). This method provides for 90% of the world's production of ammonia according to Appl (2005). The challenge is typically the production of hydrogen to be used for this process (Kirk-Othmer, 2007) with the majority of the ammonia plant dedicated to hydrogen production. In most global operations the production of hydrogen is done through steam reforming using natural gas as a feedstock. The ammonium hydroxide to be used for mineral carbonation according to the ammonium salts process will be assumed to have been provided through ammonia produced via the steam reforming route as described above.

Hydrochloric Acid

Also known as muriatic acid, this is a solution of hydrogen chloride in water. Hydrochloric acid is used to extract magnesium from the silicate mineral in the multi-stage extraction process (Lackner et al., 1995) and the indirect pH swing method used by Meyer et al. (2014). The production of hydrogen chloride occurs through synthesis from hydrogen and chlorine gases. This process occurs in an industrial burner and is considered the simplest approach (Austin and Glowacki, 2005). According to Kirk-Othmer (2007) a high purity (>99%) hydrogen chloride gas stream is produced from the burner, which can be used to manufacture pure hydrochloric acid. The direct synthesis from elements was selected as the method of production for the hydrochloric acid used in the mineral carbonation processes discussed here.

Sodium Hydroxide

This chemical compound is used to adjust the pH to alkaline conditions in the indirect HCl leach process (Meyer et al., 2014). The production of sodium hydroxide primarily occurs through the electrolysis of sodium chloride (Kirk-Othmer, 2007). Three different cell

configurations are used for this process: the mercury cell, the diaphragm cell and the membrane cell. The application of either of these technologies produces sodium concentration with the same final level of purity (Kurt and Bittner, 2005). The approach taken for the sodium hydroxide used in the mineral carbonation is to use an average of the three processes as this is allowable by the software tool used for carbon dioxide emissions accounting.

Sodium Chloride

Commonly known as salt, this compound is produced from extracting the salt by using water to dissolve it from rock salt deposits underground. The resulting brine solution is then evaporated to produce sodium chloride crystals (Kirk-Othmer, 2007). This process is known as solution mining. It is considered the modern, economical method for extracting sodium chloride from underground deposits (Westphal et al., 2005). Sodium chloride is used as an additive to the National Energy Technology Laboratory (NETL) direct aqueous carbonation process to enhance process performance (O'Connor et al., 2002; Gerdemann et al., 2007). The source of sodium chloride for this mineral carbonation process route will thus be through the solution mining process discussed.

Sodium Bicarbonate

The second additive to the direct aqueous carbonation process developed at the NETL is sodium bicarbonate. This compound is produced primarily through the use of a process implemented in 1880 called the Solvay process (Thieme, 2005). This process involves the reaction of sodium chloride with ammonia and carbon dioxide to produce sodium bicarbonate and ammonium chloride in the presence of water. Typically, this process includes a calcination step that produces sodium carbonate from sodium bicarbonate (Kirk-Othmer, 2007). The production of sodium bicarbonate for use in the direct aqueous mineral carbonation process is assumed to be through the Solvay process as has been discussed.

3.3.2 Calculation of Emissions

Impact assessment is the phase where the results of the inventory analysis are processed and interpreted in terms of environmental impacts. The impact assessment attempts to establish a link between a process and its potential environmental impact (EPA, 2006). The identification of relevant impact categories is the foremost step in the impact assessment, and is typically conducted as part of the goal and scope definition. Accordingly, the climate change impact category was considered in the analysis as has been stated in Section 3.1. This impact is defined as the impact of human emissions on radioactive forcing of the atmosphere (Guinée et al.,

2002). These emissions are measured through the emissions of greenhouse gases (CO_2, CH_4, CFCs, CO, HFCs, O_3) into the atmosphere. The accumulation of these gases in the atmosphere causes climate change. Science-based characterisation factors are used to convert and combine results into representative indicators of impacts. In the case of climate change greenhouse gas emissions associated with material and energy inputs are expressed in terms of CO_2 equivalents. This is a measure used to define greenhouse gas emissions in terms of a common unit, which is related to the heat the greenhouse gas traps relative to carbon dioxide (IPCC, 2007). This is referred to as the Global Warming Potential (GWP), and Table 3-1 shows the potentials for a 100-yr time horizon as provided by the IPCC (2007).

Table 3-1: Global Warming Potentials (GWP100) for greenhouse gases (IPCC, 2007)

Greenhouse Gas	Global Warming Potential (100-yr horizon)
Carbon Dioxide (CO_2)	1
Methane (CH_4)	25
Nitrous oxide (N_2O)	298
Hydrofluorocarbons (HFCs)	124-14800
Chlorofluorocarbons (CFCs)	4750-14400
Sulphur hecafluoride (SF_6)	22800
Nitrogen trifluoride (NF_3)	17200

The mass and energy balance results obtained on Aspen serve as a basis for analysis in terms of the CO_2 footprint that results from the material and energy requirements of the process. This analysis is conducted using SimaPro software v7.7.3. SimaPro is a product system modelling and assessment software that is widely used as a life cycle assessment tool to give an indication of the sustainability of a product or process (Herrmann and Moltesen, 2015). The software program comes integrated with a number of databases including Ecoinvent v2.2, which is the world's leading database. This database provides consistent and transparent up-to-date Life Cycle Inventory (LCI) data, and was used for assessing the impacts of heat and chemical reagents. For electricity, the South African electricity mix database developed by Dick (2012) at SASOL was used, and the ELCD database, which is integrated on SimaPro, for process water.

The approach taken for defining category indicators is the problem-oriented approach. According to Guinée et al. (2002) this approach is driven by environmental problems (midpoint) rather than by damage (endpoint). The uncertainty of results using this approach is low in comparison to the endpoint level, since category indicators are defined at midpoints

along the environmental mechanism. Hence, this approach is considered the "best available practice" (Guinée et al., 2002). A representation of the midpoint and endpoint approaches on climate change is presented in Figure 3-5.

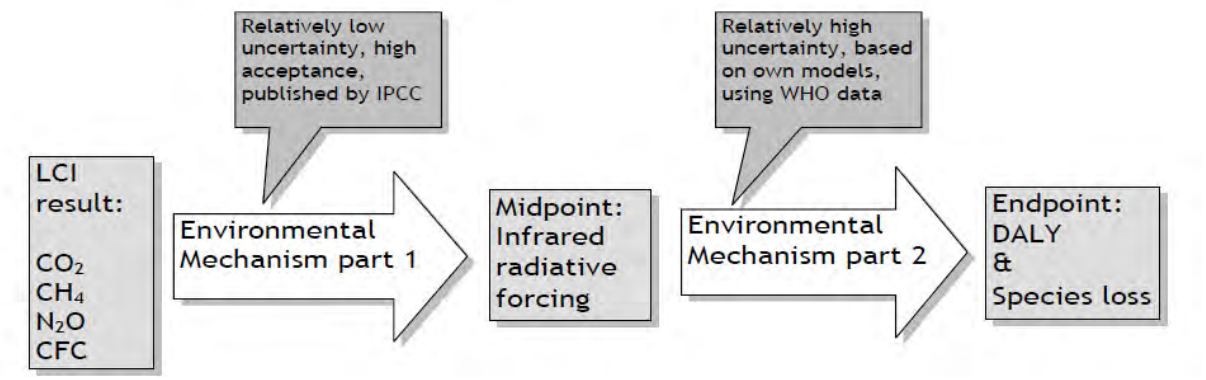


Figure 3-5: A representation of midpoint and endpoint approach to climate change (Goedkoop et al., 2013)

The ReCiPe Midpoint (H) method, which is the most frequently used, was used for impact assessment. This method uses the global warming potential as the characterisation factor for the climate change category (PRé, 2015). The carbon dioxide equivalency factors are calculated using the following equation (Goedkoop et al., 2013):

$$GWP_{x,T} = \frac{\int_0^T a_x \times [x(t)]dt}{\int_0^T a_r \times [r(t)]dt} \quad (20)$$

Where $GWP_{x,T}$ is the global warming potential of substance x over time horizon T, a_x is the radioactive efficiency due to a unit increase in atmospheric abundance of the substance in question, $[x(t)]$ is the time-dependent abundance of substance x and the corresponding quantities in the denominator being the reference gas. The factor for this method is for a 100-yr time horizon (GWP100) for each greenhouse gas emission to the atmosphere. The equivalence factors presented in the IPCC (2007) report are used as midpoint characterisation factors (Goedkoop et al., 2013) to estimate global warming potential.

The materials and energy requirements are used as input data in developed SimaPro process blocks. These blocks are developed on the basis of the considerations of the source of the particular requirement, as discussed in Section 3.3.1. The detailed outlines of SimaPro process inputs and resulting emissions are presented in Appendix D.

Chapter 4

Case Study Results

The primary aim of this study is to investigate the viability of using PGM tailings to sequester CO_2 from the perspective of an overall CO_2 balance across the entire process. The results obtained from the evaluation of selected mineral carbonation process routes are presented in this Chapter. Mass and energy balance calculations were conducted on selected carbonation processes, through which the carbon dioxide footprints of these processes were then evaluated. As discussed in Chapter 3, pyroxene was used as a proxy for PGM tailings and, in the absence of available experimental data, conversions derived from stoichiometric equations and assumed efficiencies. On this basis, material requirements for processes are presented, on which energy calculations were based. The energy requirements of individual units are then presented, which identify the major energy consuming units. To conduct the mass and energy balances, AspenPlus simulation software was used as detailed in Section 3.2. It is important to note that the reactor conversions referred to in this Chapter are single pass conversion of materials as they pass the reactor. The overall conversions for the process have been attached in Appendix F. Finally, results on the CO_2 footprint of the process are presented. These results were generated using material and energy balance data processed through SimaPro software, to give carbon dioxide footprints as described in Section 3.3.

4.1 Ammonium Salts Process

4.1.1 Flowsheet Description and Mass Balance

The ammonium salts process involves the use of ammonium salts based reagents to extract and carbonate metal cations and also to capture CO_2. The key chemical reactions occurring are presented in Table 4-1, and a simplified version of the flowsheet and material balance for the ammonium salts process is presented in Figure 4-1. This diagram indicates the key flows within the process, as well as the key unit operations that make up the process, for the sake of clarity and simplicity. It does not represent all the flows through the process. This is the case for all processes discussed in this Chapter. Detailed material balances and the Aspen Plus simulation diagram for this process are attached in Appendix B and E, respectively.

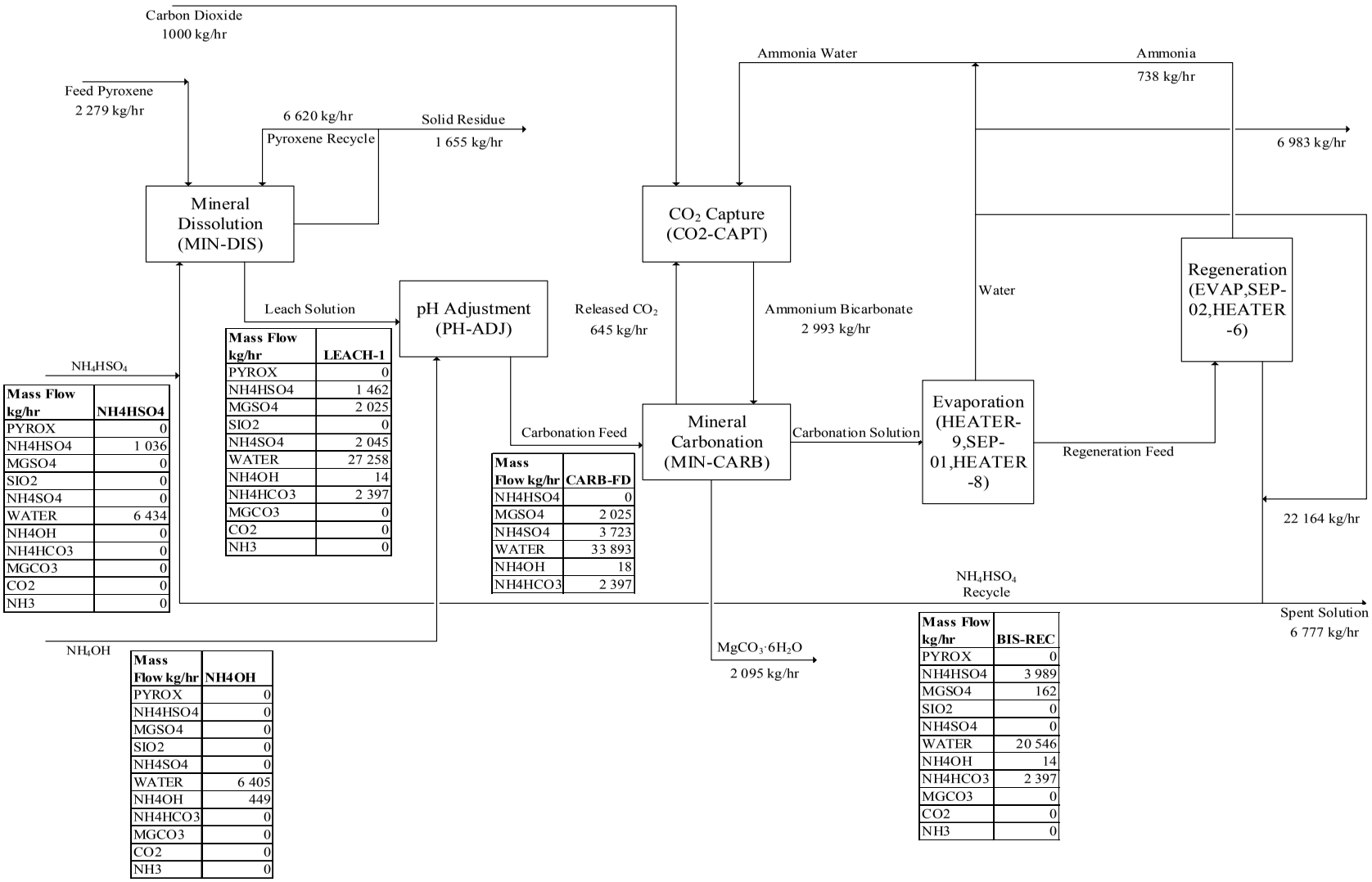
Table 4-1: Chemical reactions occurring in the ammonium salts process

Reactor Unit	Chemical Reaction	T (°C)	P (atm)
Mineral Dissolution	$MgSiO_3+2NH_4HSO_4 \rightarrow MgSO_4+SiO_2+(NH_4)_2SO_4+H_2O$	90	1
pH Adjustment	$NH_4HSO_4+NH_4OH \rightarrow (NH_4)_2SO_4+H_2O$	25	1
Mineral Carbonation	$MgSO_4+NH_4HCO_3+H_2O \rightarrow MgCO_3 \cdot 6H_2O+(NH_4)_2SO_4+CO_2$	80	1
CO_2 Capture	$CO_2+NH_3+H_2O \rightarrow NH_4HCO_3$	10	1
Regeneration	$(NH_4)_2SO_4 \rightarrow NH_3+NH_4HSO_4$	300	1

Some aspects of this discussion will refer to streams that have been presented only on the simulation diagram attached in the appendices. Simulations for this process were run for extraction efficiencies of 30%, 50% and 90%, which represent the literature extraction efficiency, a gradual improvement in this efficiency as well as an optimistic substantial improvement, respectively. The carbonation efficiency was held at 90%, as suggested in literature (Wang and Maroto-Valer, 2013). The mass balance presented in Figure 4-1 is for a process that sequesters 1 000 kg/hr of carbon dioxide at 30% extraction efficiency and 90% carbonation efficiency, per pass.

Ammonium bisulphate and the silicate mineral are first preheated to the reaction temperature, 90 °C, prior to being fed into the dissolution reactor (MIN-DIS). In this reactor, 30% conversion of the pyroxene fed in to the reactor, through reaction with ammonium bisulphate, produces 2 025 kg/hr of magnesium sulphate. The resultant slurry of leach solution, unreacted mineral and silica is then separated in a solid-liquid separation unit (SIO2-SEP). This splits the slurry stream into two streams, a solids stream of which 80% (6 620 kg/hr) is recycled (SIO2-PYR) and a solution containing magnesium ions (LEACH-1), to improve the overall conversion of pyroxene.

The mineral dissolution unit produces 2 025 kg/hr of magnesium sulphate in a solution containing excess ammonium bisulphate (1 461 kg/hr) that needs to be neutralised and pH adjusted using ammonium hydroxide prior to carbonation. Upon pH adjustment, which occurs at 25 °C, the solution, now referred to as LEACH-3, is preheated to the carbonation reaction conditions (80 °C, 1 atm). Another stream, the ammonium bicarbonate stream (NH4-HCO3) is also fed (after preheating) into the carbonation reactor (MIN-CARB). This stream carries 2 993 kg/hr of ammonium bicarbonate produced during CO_2 capture. It is the carbon dioxide carrier, providing the essential ingredient required for carbonation.



Mass Flow kg/hr	NH4HSO4
PYROX	0
NH4HSO4	1 036
MGSO4	0
SIO2	0
NH4SO4	0
WATER	6 434
NH4OH	0
NH4HCO3	0
MGCO3	0
CO2	0
NH3	0

Mass Flow kg/hr	LEACH-1
PYROX	0
NH4HSO4	1 462
MGSO4	2 025
SIO2	0
NH4SO4	2 045
WATER	27 258
NH4OH	14
NH4HCO3	2 397
MGCO3	0
CO2	0
NH3	0

Mass Flow kg/hr	CARB-FD
NH4HSO4	0
MGSO4	2 025
NH4SO4	3 723
WATER	33 893
NH4OH	18
NH4HCO3	2 397

Mass Flow kg/hr	BIS-REC
PYROX	0
NH4HSO4	3 989
MGSO4	162
SIO2	0
NH4SO4	0
WATER	20 546
NH4OH	14
NH4HCO3	2 397
MGCO3	0
CO2	0
NH3	0

Mass Flow kg/hr	NH4OH
PYROX	0
NH4HSO4	0
MGSO4	0
SIO2	0
NH4SO4	0
WATER	6 405
NH4OH	449
NH4HCO3	0
MGCO3	0
CO2	0
NH3	0

Figure 4-1: Ammonium salts process material balance at 30% extraction efficiency

The carbonation reaction produces solid hydromagnesite (2 095 kg/hr) from the reaction of magnesium sulphate and ammonium bicarbonate. This reaction also produces CO_2 as a bi-product, which is undesired since the process is designed to sequester carbon dioxide. To resolve this a closed CO_2-loop was implemented by sending this carbon dioxide (CO2, CO2-streams) to the capture unit.

The second stream (referred to as the "Carbonation Solution" in Figure 4-1) carries a solution rich in ammonium sulphate which is produced during dissolution, pH adjustment and carbonation. This stream also carries large quantities of water that have to be evaporated prior to thermal decomposition to regenerate reagents. During evaporation the stream is heated up to 120 °C (HEATER-9) to drive-off water as steam, leaving solid ammonium sulphate. Most of the water is condensed (HEATER-8) and used in the process mixing it with ammonia for CO_2 capture and using it to dissolve regenerated ammonium bisulphate. About 7 000 kg/hr is removed from the system to reduce the need to evaporate water that is not essential to the process.

The stream ("Regeneration Feed") carries solid crystals of ammonium sulphate that are to be decomposed, thermally, to regenerate ammonia and ammonium bisulphate. This is achieved in the thermal decomposition reactor (EVAP) that operates at 300 °C. This results in the production of 738 kg/hr ammonia and 4 986 kg/hr ammonium bisulphate from 5 724 kg/hr ammonium sulphate. Prior to being separated (SEP-02), the product stream (DEC-PRD) is cooled to 90 °C. The separator removes ammonia which is fed to the capture unit (CO2-CAPT), and the RECYCLE stream, which consists of regenerated ammonium bisulphate, is sent for mixing with water.

The ammonia is used in carbon dioxide capture whereas 80% of the ammonium bisulphate carrying stream (BIS-REC) is recycled and 20% becoming spent solution. This removes excess water and reagents (like ammonium bicarbonate) as well as carrying small amounts of unreacted magnesium sulphate. A trade-off is made in the purging this quantity of reagent since increasing the recycle may reduce external material requirements, whilst potentially increasing recycle sizes and unit energy requirement.

The CO_2 capture unit, operating at 10 °C and 1 atm, uses ammonia and water to capture CO_2. Condensed water from the evaporation circuit is fed alongside regenerated ammonia to produce an aqueous stream that captures 1 000 kg/hr of feed carbon dioxide, plus the carbon dioxide

produced by the carbonation reaction. This produces the ammonium bicarbonate stream that is used as the CO_2-carrier in the carbonation reaction.

The overall material requirements of the ammonium salts process are presented in Table 4-2. These indicate the feed input or make-up for regenerated components that would need to be supplied to the process. Since the process was developed with multiple recycle streams for key reagents and pyroxene, the material requirements are expected to be less than the stoichiometric requirements. For example, from a stoichiometric point of view the feed requirements of ammonium bisulphate required to extract magnesium from the silicate mineral is twice the amount of pyroxene input. This could imply that at least 5 225 kg/hr of ammonium bisulphate fresh feed would be required instead of about 1 100 kg/hr fresh feed this process requires. This is a significant reduction in material requirements. It highlights the importance of recycle streams and regeneration in mineral carbonation operations like the ammonium salts process. The benefit from this would be a reduced environmental footprint associated with reagent procurement, and could additionally lower the raw material cost of operating the ammonium salts process.

Table 4-2: Material requirements for ammonium salts carbonation

	Mass Flow (kg/hr)		
Component	30% Extraction	50% Extraction	90% Extraction
Carbon Dioxide	1 000	1 000	1 000
Pyroxene	2 279	2 279	2 279
Ammonium Bisulphate	1 036	1 036	1 151
Ammonium Hydroxide	526	280	210
Water	13 940	10 437	10 151

4.1.2 Process Energy Requirements

Figure 4-2 indicates the energy requirements of major process units in the ammonium salts carbonation process. This figure shows exothermic unit operations (negative energy requirements) and endothermic unit operations (positive energy requirements). The sensitivity of energy requirements of process units to changes in extraction efficiency is also demonstrated. A majority of the unit operations in the ammonium salts process require or generate less than 10 000 MJ/hr. The mineral dissolution (MIN-DIS), pH adjustment (PH-ADJ) and CO_2 capture (CO2-CAPT) units are the only non-heater units that release energy, whereas the carbonation (MIN-CARB) and thermal decomposition (EVAP) units require energy. However, two process units stand out as major energy consuming or generating (HEATER-8,

HEATER-9). These are the condenser that cools steam released during evaporation and the evaporator that drives-off water to facilitate the crystallization before thermal decomposition of ammonium sulphate, respectively. The evaporator in particular requires at least ten times more energy than the second highest energy consuming unit. This is because of the large quantities of water that need to be evaporated, as indicated in Table 4-2 and the energy balance around this unit presented in Appendix C.

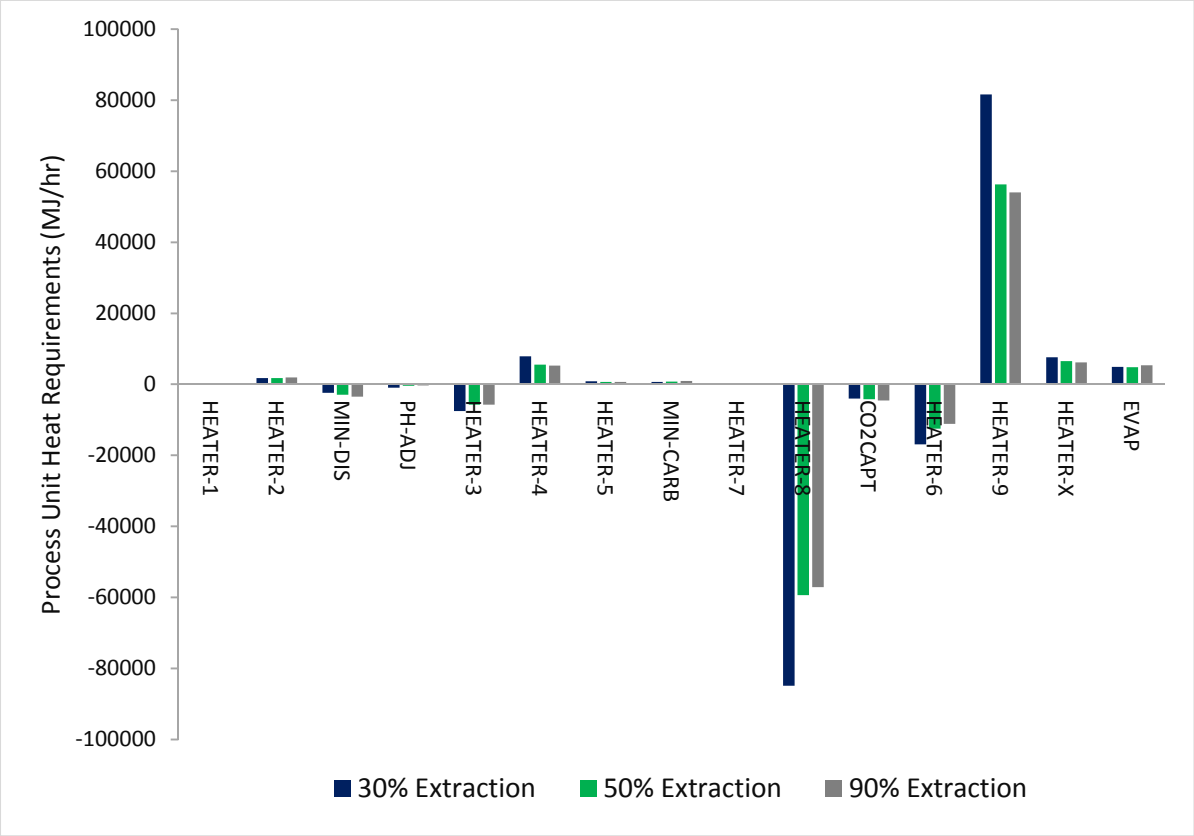


Figure 4-2: Energy requirements for major process units in the ammonium salts process

This observation is consistent with work carried out by Dri (2014) on the feasibility of the sequestration of steel plant CO_2 emissions through the use of the ammonium salts process and steel slag. Though this study used a calcium-based feedstock, and HSC Chemistry Software (which does not have the ELECNRTL electrolyte property method for energy balances), the findings are qualitatively comparable. The authors found that the biggest energy demand was the evaporation of water prior to decomposition and that most key unit operations (mineral dissolution, CO_2 capture, pH adjustment) were exothermic. However, they found carbonation to be slightly exothermic in comparison to slightly endothermic as indicated in Figure 4-2. This discrepancy could be a result of different carbon dioxide carriers used, since ammonium carbonate is used in the process studied by the authors instead of ammonium bicarbonate. The

study by Dri (2014) is the only study known that evaluates the energy requirements of a process that implements the ammonium salts approach.

The total amount of energy required by the process ranges from about 75 000 MJ/hr to 105 000 MJ/hr from the highest to lowest extraction efficiency. This is a significant amount of energy that could potentially result in substantial carbon dioxide penalties, as will be shown in Section 4.1.3. Identifying opportunities for heat integration appears to be a potential solution to reduce heat requirements, since the ammonium salts process also has a notable number of exothermic process units, for example HEATER-8, that release significant quantities of energy. Additionally some authors have suggested the use of a mechanical vapour recompression (MVR) evaporator that uses less energy than conventional evaporation (Dri, 2014).

It can also be noted that the amount of energy required for the process units generally decreases with increasing extraction efficiency. This is to be expected since an increase in extraction efficiency reduces the quantities of materials flowing through the units due to reduced sizes of recycle streams (Appendix B). This suggests that increasing the extraction efficiency could be beneficial towards reducing the overall heat requirements, as well as potentially reducing the size of process units due to the smaller recycle streams.

4.1.3 Carbon Dioxide Footprint

The material and energy requirements can be converted to process CO_2 footprint through the use of SimaPro inventory analysis software. The inputs to this software are the material and energy requirements calculated from simulation through Aspen Plus. Table 4-3 indicates the individual contributions of process requirements to the overall carbon footprint of the ammonium salts process.

Table 4-3: Process contributions to carbon dioxide footprint (kg-CO_2e)

Description	30% Extraction	50% Extraction	90% Extraction
Compression	60	60	60
Heat Requirements	7 541	5 484	5 333
Ammonium Bisulphate	695	695	772
Ammonium Hydroxide	418	183	121
Process Water	84	60	59
Total Footprint	8 798	6 482	6 346

Figure 4-3 presents the carbon dioxide footprint of the ammonium salts process system. The results presented indicate a breakdown of the footprint, outlining the contributions of individual

process inputs to the overall process footprint. Additionally, the effect of extraction efficiency in the dissolution stage on the carbon dioxide footprint is also presented.

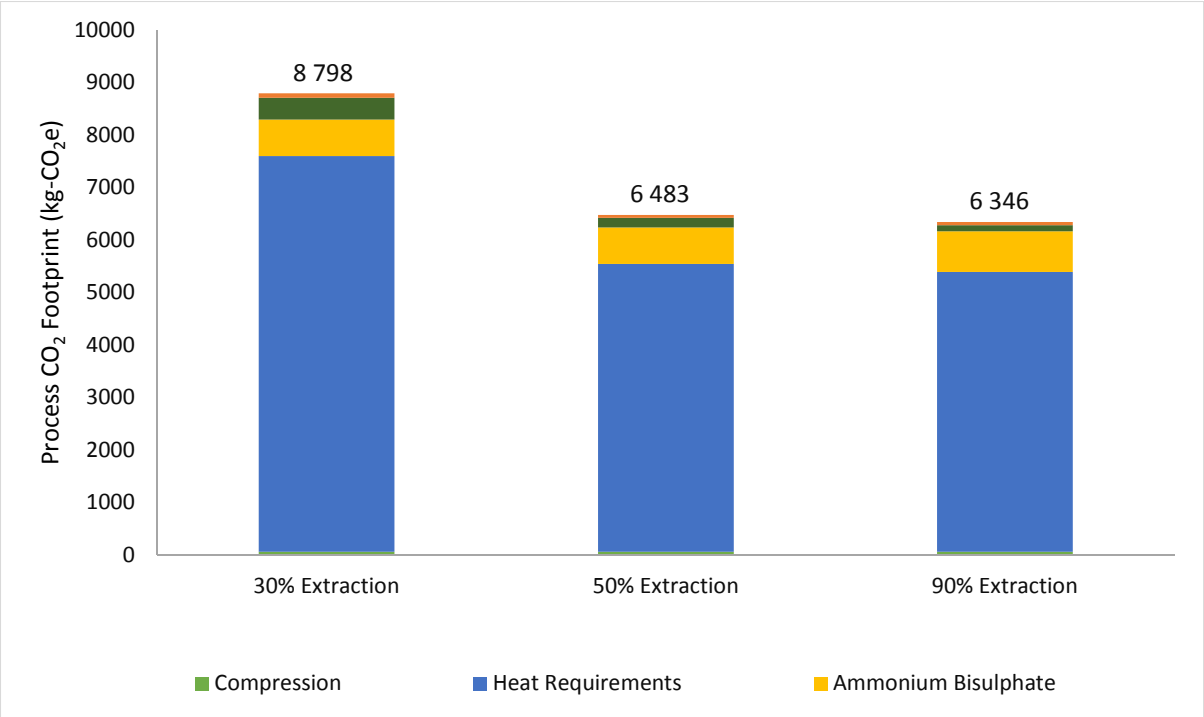


Figure 4-3: CO_2 footprint of material and energy requirements of ammonium salts process (kg-CO_2e)

It can be noted from this figure that the overall footprint well exceeds the 1 000 kg of CO_2 the process is designed to sequester, regardless of the extraction efficiency. The carbon dioxide footprint is more than 8 times greater than the carbon dioxide the process can sequester.

The most emissions intensive component of this mineral carbonation system is process heat generation. This accounts for about 85% of the total carbon dioxide emissions of the ammonium salts process. This observation has also been made by other authors (Dri, 2014, Sanna et al., 2014b) who have even suggested the implementation of a sodium salts-based process (Sanna et al., 2014c), of which the regeneration step is suggested to use a third of the energy in comparison to ammonium salts regeneration. However, the technical feasibility of the regeneration step is yet to be established, for the sodium salts-based process.

An option to consider could be exploring heat integration opportunities. Considering that the heat requirements will probably have to be reduced by at least 85%, this implies that a similar percentage saving will be required from the heat exchanger network design. The heat exchanger network is unlikely to achieve this target due to thermodynamic limitations as well as heat losses. This suggests that heat integration in isolation is not enough to bring the process towards at the least carbon neutrality. The more reasonable approach would be to focus efforts

on developing an alternate low-temperature regeneration process for this mineral carbonation system. (Dri, 2014) has also suggested that reducing the amount of water, thereby increasing the S/L ratio, may reduce the energy requirements without affecting reaction performance. However, findings from another study have indicated that reducing the S/L ratio may negatively affect extraction efficiency (Wang, 2011).

However, it must also be noted that the sum of the other contributions, excluding heat, also exceed 1000 kg-CO_2e. This is primarily due to ammonium bisulphate and ammonium hydroxide production, to supply fresh feed to the process, which represent 695 kg-CO_2e and 418 kg-CO_2e, respectively. The amount of fresh reagent feed can be lowered by increasing the recycle ratio, however this could potentially increase heat requirements and also present challenges with regards to process control since this can result in much greater "snowball effects" when disturbances occur (Svrcek et al., 2006).

The results in Figure 4-3 also indicate that the carbon dioxide footprint decreases with an increase in extraction efficiency. This decrease, though sizable, is not sufficient to reduce the carbon dioxide footprint below the CO_2 threshold of 1 000 kg/hr. This demonstrates that increasing extraction efficiency (which may require increasing reaction temperatures) does not yield enough of a benefit worth pursuing, in the current process configuration. Another potential carbon impact could be the ammonium bicarbonate leaving the process through the spent solution stream in Figure 4-1. As noted earlier (Section 4.1.1) and demonstrated in Table 4-1, this component is the carbon dioxide carrier in this process for carbonation, and thus would be expected to be carrying away some of the carbon dioxide that should have been sequestered. However, since post-processing of products is outside the scope of this study, this impact was not included.

4.2 Lackner's HCl Multistage Process

4.2.1 Flowsheet Description and Mass Balance

This process involves the extraction and conversion of magnesium in the silicate mineral to magnesium hydroxide through using hydrochloric acid as leaching agent, and multiple subsequent conversion steps. This process is based on a concept for a carbonation process proposed by Lackner et al. (1995). Experimental work related to this process was not conducted by the authors.

Similar to the ammonium salts process, simulations for this process were conducted for 30%, 50% and 90% dissolution. A material balance for this process is presented in Figure 4-4 for

30% extraction of magnesium ions from pyroxene and the chemical reactions occurring are presented in Table 4-4. Detailed mass balances and Aspen Plus simulations are presented in Appendix B and E, respectively.

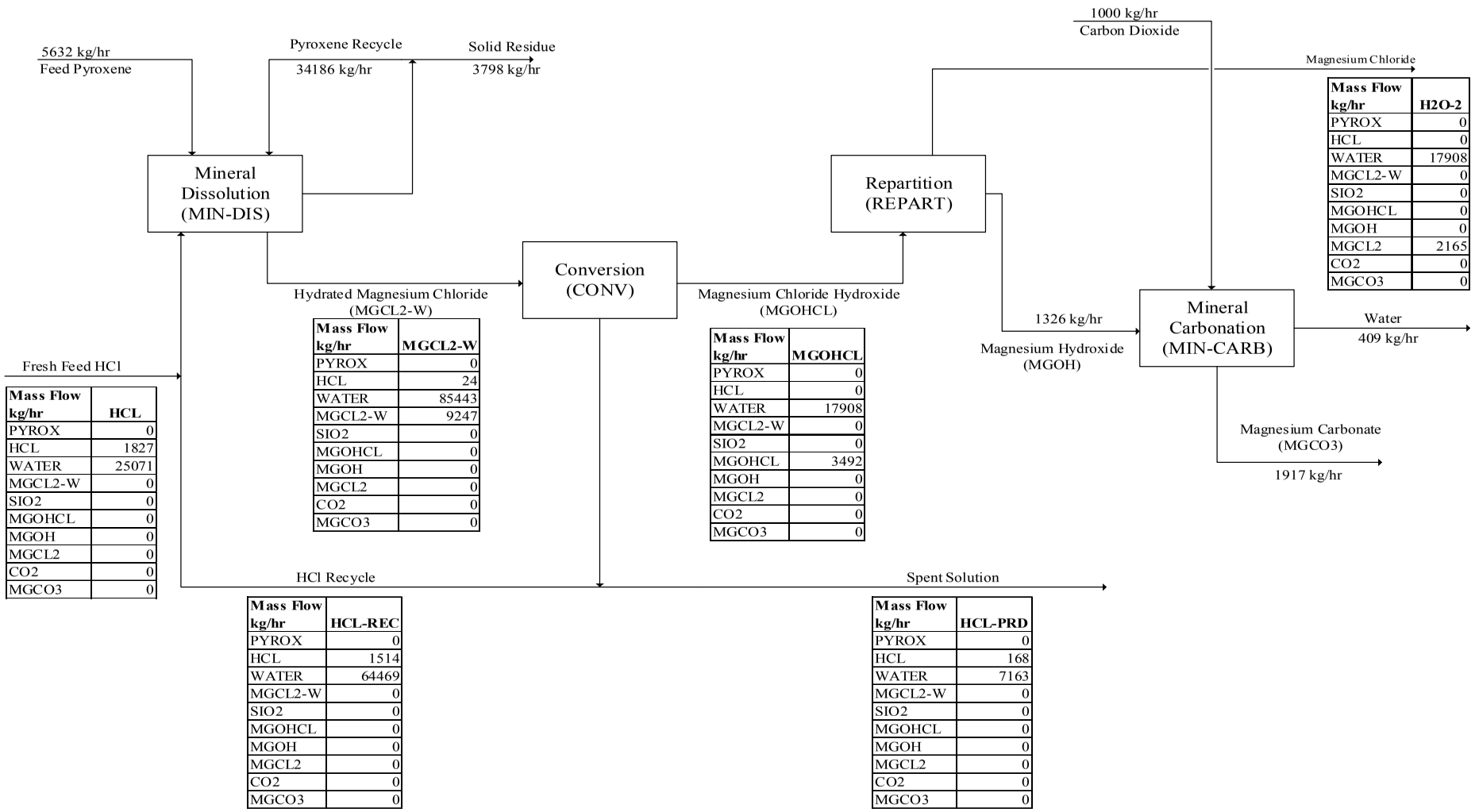
Table 4-4: Chemical reactions occurring in Lackner's HCl multi-stage process

Reactor Unit	Chemical Reaction	T (°C)	P (atm)
Mineral Dissolution	$MgSiO_3+HCl+5H_2O \rightarrow MgCl_2 \cdot 6H_2O+SiO_2$	70	1
Conversion	$MgCl_2 \cdot 6H_2O \rightarrow MgOHCl+HCl+5H_2O$	150	1
Repartition	$2MgOHCl \rightarrow Mg(OH)_2+MgCl_2$	25	1
Mineral Carbonation	$Mg(OH)_2+CO_2 \rightarrow MgCO_3+H_2O$	407	1

The silicate mineral (pyroxene) and HCl solution are fed into preheaters where they are heated to 70 °C, the dissolution reactor operating temperature. These are then fed into the reactor where magnesium is extracted from the silicate mineral matrix to produce 9 247 kg/hr of hydrated magnesium chloride ($MgCl_2 \cdot 6H_2O$).

The reaction products and unreacted reagents form a slurry that is then separated through solid-liquid separations with unreacted solids (90% of solids stream) recycled back to the dissolution reactor (MIN-DIS), to improve the overall conversion of the silicate mineral, pyroxene. On the other hand, the separated solution is fed into the conversion process where $MgCl_2 \cdot 6H_2O$ is converted to 3 492 kg/hr Mg(OH)Cl at 150 °C. This conversion process also regenerates acid when $MgCl_2 \cdot 6H_2O$ initially loses the chemically bound water, with HCl eventually separating out instead of additional water release. A majority (1 514 kg/hr) of the regenerated acid is sent back to the mineral dissolution reactor as recycle. It is assumed that 10% removed accounts for losses and spent solution.

The Mg(OH)Cl produced is then fed into the repartitioning unit where, in the presence of water, the chemical is converted to produce 1 326 kg/hr $Mg(OH)_2$ and 2 166 kg/hr $MgCl_2$. The exiting magnesium chloride stream also serves as an outlet for water, which accumulates in the system. This avoids circulating large quantities of water which have no role in the process and could potentially increase unit capacities and heat requirements. The $Mg(OH)_2$ produced is then carbonated with gaseous carbon dioxide to produce 1 916 kg/hr magnesium carbonate, at 407 °C.



Mass Flow kg/hr	HCL
PYROX	0
HCL	1827
WATER	25071
MGCL2-W	0
SIO2	0
MGOHCL	0
MGOH	0
MGCL2	0
CO2	0
MGCO3	0

Mass Flow kg/hr	MGCL2-W
PYROX	0
HCL	24
WATER	85443
MGCL2-W	9247
SIO2	0
MGOHCL	0
MGOH	0
MGCL2	0
CO2	0
MGCO3	0

Mass Flow kg/hr	MGOHCL
PYROX	0
HCL	0
WATER	17908
MGCL2-W	0
SIO2	0
MGOHCL	3492
MGOH	0
MGCL2	0
CO2	0
MGCO3	0

Mass Flow kg/hr	H2O-2
PYROX	0
HCL	0
WATER	17908
MGCL2-W	0
SIO2	0
MGOHCL	0
MGOH	0
MGCL2	2165
CO2	0
MGCO3	0

Mass Flow kg/hr	HCL-REC
PYROX	0
HCL	1514
WATER	64469
MGCL2-W	0
SIO2	0
MGOHCL	0
MGOH	0
MGCL2	0
CO2	0
MGCO3	0

Mass Flow kg/hr	HCL-PRD
PYROX	0
HCL	168
WATER	7163
MGCL2-W	0
SIO2	0
MGOHCL	0
MGOH	0
MGCL2	0
CO2	0
MGCO3	0

Figure 4-4: Material balance for Lackner's multi-stage process for 30% extraction efficiency

The overall material requirements for this process are presented in Table 4-5, and indicate that a substantial amount of pyroxene is required for the sequestration in this process, at about 5.6 times the carbon dioxide sequestered, by mass. This implies that larger size vessels would have to be designed to handle this material throughout the process. Similarly, recycle streams were implemented into this process which explain the lower fresh hydrochloric acid input, from a stoichiometry point of view. Since the design of the process is such that the feed into the reactor is sufficient from a stoichiometric perspective, through the use of recycle streams, the consequence is that as the extraction efficiency increases, the amount of fresh hydrochloric acid increases. Since the recycle ratio is kept constant in all simulations, the additional reagent for the increased conversion will have to come from increasing the fresh hydrochloric acid input.

Table 4-5: Material requirements for Lackner's HCl multi-stage process

	Mass Flow (kg/hr)		
Component	30% Extraction	50% Extraction	90% Extraction
Carbon Dioxide	1 000	1 000	1 000
Pyroxene	5 632	5 632	5 632
Hydrochloric Acid	1 827	2 049	2 228
Water	25 071	28 124	30 576

4.2.2 Process Energy Requirements

The energy requirements of individual process units are presented in Figure 4-2. A majority of the unit operations (including mineral dissolution and carbonation) in this process require or release comparatively modest amounts of energy, with the exception of the conversion (CONV) and cooling (HEATER-4) process units. The conversion unit is the operation whereby high temperatures are used to drive off water and regenerate acid, in the process converting hydrated magnesium chloride to Mg(OH)Cl. This process, carried out at 150 °C, requires substantial amounts of energy to drive off large quantities of water. On the other hand, a notable amount of heat is released during cooling in the unit (HEATER-4). This unit condenses evaporated water and acid produced during the conversion process. The energy carried by the evaporated products could potentially be used to pre-heat prior to conversion, though it is anticipated that not all this energy will be recovered. The results obtained are not unexpected since findings made by Newall et al. (2000) pointed to evaporation as a major energy consumer. In fact, the authors established that the process energy requirements were four times that which is produced by the plant producing the emissions that the process was intended to sequester.

The total amount of energy required rises from 230×10^3 MJ/hr to 280×10^3 MJ/hr, whereas the energy released rises from -183×10^3 MJ/hr to -223×10^3 MJ/hr with increasing extraction efficiency.

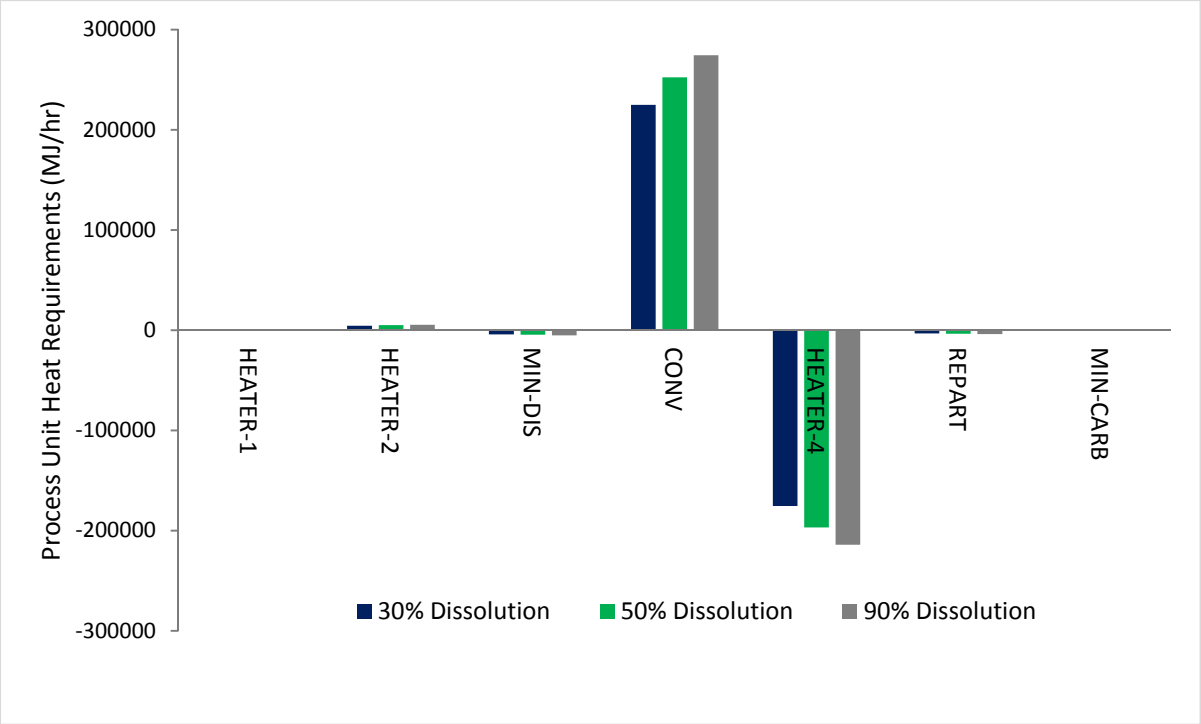


Figure 4-5: Energy requirements for major process units in the Lackner's HCl multi-stage process

An interesting observation is the increase in the energy requirements with increasing extraction efficiency. This can be attributed to the increase in fresh hydrochloric acid required with an increase in conversion. To illustrate this, we see a 12% increase in total energy requirements (from 230×10^3 MJ/hr to 258×10^3 MJ/hr) with a 12% increase in hydrochloric acid requirement indicated in Table 4-5. The increase in fresh hydrochloric acid can be expected because the recycle ratio in all simulations is held constant, thus additional reagent to account for the increase in conversion will have to come from increasing the fresh reagent feed to meet stoichiometric requirements.

4.2.3 Carbon Dioxide Footprint

The energy and material requirements of the process translate to a carbon dioxide footprint associated with attaining these resources. The results presented in Table 4-6 and Figure 4-6 indicate a breakdown of contributions of different process inputs to the overall carbon footprint of the process. It also demonstrates the impact of increasing extraction efficiency on the carbon dioxide emissions attributed to the process. It is evident from the total footprint (18.3 – 22.3

ton-CO_2e) that the emissions released by the process are way above the emissions the process has potential to sequester (1 ton of CO_2).

Table 4-6: Process contributions to carbon dioxide footprint (kg-CO_2e)

Description	30% Extraction	50% Extraction	90% Extraction
Compression Electricity	60	60	60
Heat Requirements	15 677	17 587	19 123
Hydrochloric Acid	2 394	2 686	2 920
Water	163	183	199
Total Footprint	18 295	20 516	22 303

About 98% of the total CO_2 footprint for the process can be attributed to heat requirements and production of fresh hydrochloric acid feed. A significant portion of this can be ascribed to heat requirements, which account for 85.7% (15.7 ton-CO_2e) of the total carbon footprint when considering the base case. This footprint is linked to the large amounts of energy required in the conversion and regeneration stage, where water is evaporated, as discussed in Section 4.2.2. It is clear that without significant reduction of this component of the footprint the sustainability of this process, from a carbon balance perspective, in its current configuration is untenable.

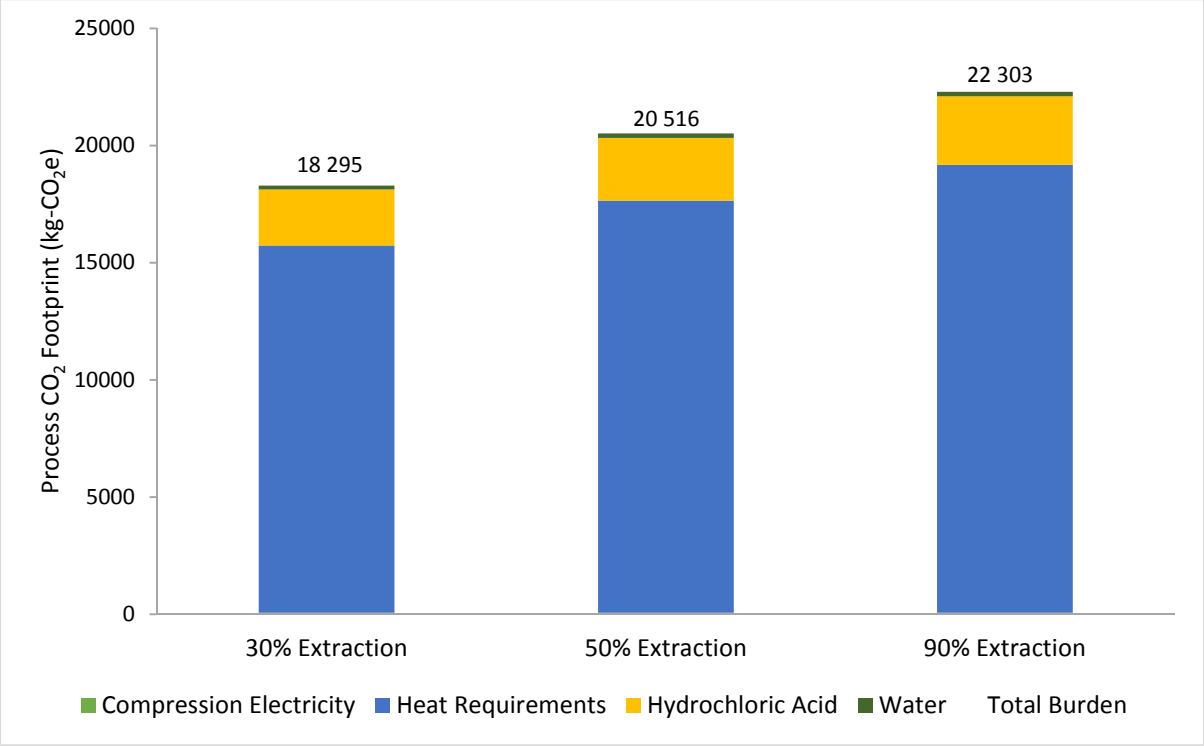


Figure 4-6: CO_2 footprint of material and energy requirements of Lackner's HCl multi-stage process (kg-CO_2e)

Additionally, the second largest carbon dioxide emissions contribution, the production of fresh hydrochloric acid feed, is at least 2.4 ton-CO_2e for every 1 ton of carbon dioxide sequestered. This indicates that, in addition to heat requirements, the process also incurs prohibitive material requirements. The primary reason for this is the energy intensive operations that are used in the production of hydrochloric acid from hydrogen and chlorine. This means that an alternative source of hydrochloric acid may have to be considered, or a reduction in the amount of fresh feed required through increasing the recycle ratio, though this may impact plant sizing and process stability (Svrcek et al., 2006).

Similar to observations made in the discussion on process energy requirements (Section 4.2.2), the carbon dioxide footprint increases with increasing extraction efficiency. This can also be accounted for by the increase in fresh hydrochloric acid feed with increasing extraction efficiency because an equivalent percentage increase in the footprint is observed.

In order to bring the process towards carbon neutrality, a reduction in emissions of at least 95% would be required. Perhaps one would consider reducing these emissions through heat integration and mass balance optimisation (for example, using highly concentrated hydrochloric acid and/or increasing recycle ratios). This required reduction in emissions is quite considerable. It is greatly optimistic to expect that such emissions reduction targets may be achieved solely by this approach without significantly affecting the operability of the process.

4.3 Åbo Akademi University (AAU) Process

4.3.1 Flowsheet Description and Mass Balance

This is a multi-stage process that makes use of an ammonium salt (ammonium sulphate) to convert magnesium in the silicate mineral to the more reactive $Mg(OH)_2$ compound through a series of unit operations. It is based on work conducted at the Åbo Akademi University (Fagerlund et al., 2010; Nduagu et al., 2012a/b; Nduagu, 2012). These authors have conducted experiments as well as evaluated the process from a life cycle perspective in a comparative study (Nduagu et al., 2012b).

The simulations for the ÅAU process were developed for two different extraction and carbonation efficiencies that will be described as Scenario 1 and Scenario 2. These represent cases where, for Scenario 1, extraction efficiency is 66% and carbonation efficiency is 55% whereas for Scenario 2, the extraction efficiency is 100% and carbonation efficiency is 80%. These scenarios are based on literature, where the maximum extraction and carbonation

efficiencies currently obtainable are described by Scenario 1, and Scenario 2 describes conditions for a simulation developed at ÅAU (Nduagu et al., 2012a).

The key chemical reactions occurring are presented in Table 4-7, and a material balance for this process presented in Figure 4-7 for Scenario 1. Detailed mass balances and Aspen Plus simulations are presented in Appendix B and E, respectively.

Table 4-7: Key reactions occurring in the Åbo Akademi University process

Reactor Unit	Chemical Reaction	T (°C)	P (atm)
Mg-Extraction	$MgSiO_3+(NH_4)_2SO_4 \rightarrow MgSO_4+SiO_2+2NH_3+H_2O$	400	1
Precipitation	$MgSO_4+2NH_3+2H_2O \rightarrow Mg(OH)_2+(NH_4)_2SO_4$	40	1
Mineral Carbonation	$Mg(OH)_2+CO_2 \rightarrow MgCO_3+H_2O$	450	19.74

The silicate mineral feedstock, pyroxene, flowing at 2 560 kg/hr is preheated to reaction conditions (400 °C, 1 atm) before being fed into the reactor (AS-REAC) where it reacts with ammonium sulphate. This reaction produces 2 919 kg/hr of magnesium sulphate ($MgSO_4$) alongside ammonia (NH_3), water (H_2O) and silicon dioxide (SiO_2). The ammonia and water, produced in gaseous form, are separated from the solid product and cooled to 25 °C. On the other hand the solids stream (SOLIDS) is also cooled.

The solids stream is subsequently mixed with 848 kg/hr of water that dissolves $MgSO_4$ produced in the extraction reactor (AS-REAC). This operation also allows for the solid-liquid separation of unreacted solids, that can then be recycled back to the extraction unit. The magnesium sulphate solution is then fed into a precipitation unit (PRECIP) that uses the cooled and condensed NH_3-H_2O stream to precipitate 1 414 kg/hr of $Mg(OH)_2$, and at the same time regenerating ammonium sulphate (AS), at 40 °C and 1 atm. This magnesium hydroxide is to be used in the carbonation unit whereas the regenerated sulphate salt (AS) will be used in the extraction unit.

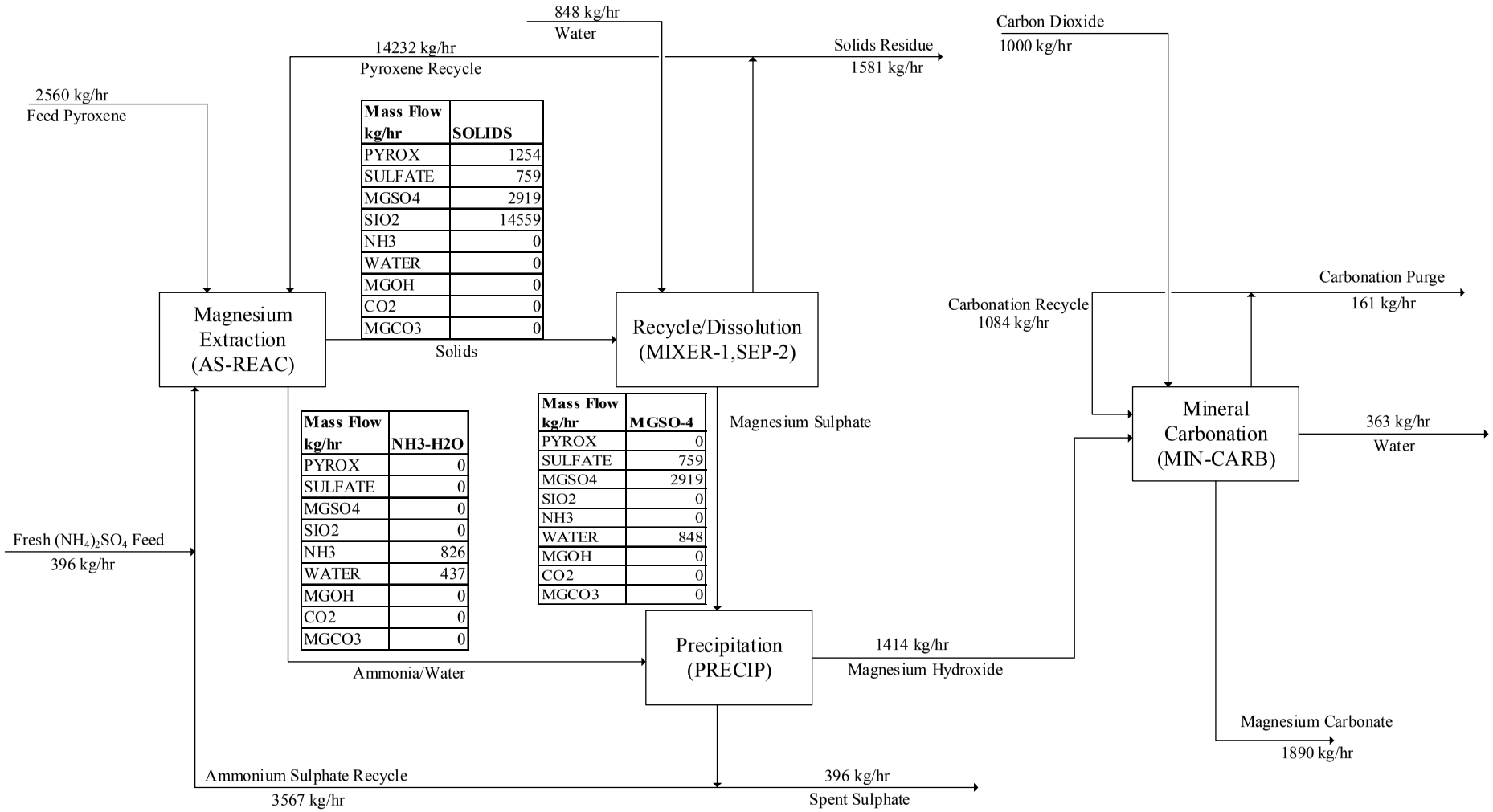


Figure 4-7: Material balance for Åbo Akademi University process for 60% extraction efficiency and 55% carbonation efficiency

The precipitated $Mg(OH)_2$ is then separated from the sulphate solution and preheated (HEATER-5) to carbonation conditions. It then enters the mineral carbonation unit (MIN-CARB) where it reacts with a feed of 1 000 kg/hr CO_2 at 450 °C and 20 bar. This unit produces a stable magnesium carbonate ($MgCO_3$) compound flowing at 1 890 kg/hr, alongside water. These products are then separated to produce a pure $MgCO_3$ stream that is cooled to 30 °C by the unit HEATER-2. After a series of separation steps, 90% of unreacted components are fed back into the mineral carbonation unit.

The AS solution produced by the precipitation unit is sent through a series of unit operations that remove water, such that the AS crystallises, making it suitable for recycle to the AS reactor. 90% of the stream (3 567 kg/hr) is fed back into the extraction unit whereas 10% is assumed to account for spent sulphate and losses. The use of recycle streams in this process increases the overall conversion from single pass, and optimises material use, in the process lowering fresh feed requirements, that cost money and carbon dioxide emissions associated with their production.

The process requires about 2.3 tons of pyroxene to sequester a ton of carbon dioxide, as indicated in Table 4-8. This process also requires relatively small amounts of ammonium sulphate fresh input. This is because of the use of recycle streams to feed the AS-REAC (see Appendix D) reactor with regenerated ammonium sulphate, as a result significantly reducing external reagent requirements. This process requires notably smaller quantities of water in comparison to the aqueous-based extraction processes. This is because the extraction reaction using ammonium sulphate occurs in a gas-solid reaction rather than in aqueous medium.

Table 4-8: Material requirements for Åbo Akademi University process

	Mass Flow (kg/hr)	
Component	Scenario 1	Scenario 2
Carbon Dioxide	1 000	1 000
Ammonium Sulphate	396	396
Pyroxene	2 560	2 281
Water	848	848

4.3.2 Process Energy Requirements

The energy requirements of major unit operations involved in the ÅAU process are presented in Figure 4-8. These results also show the impact of an improvement in efficiencies of the extraction and carbonation stages. The process has an even spread of energy consuming and

releasing units, that generally are below 2 000 MJ/hr. Most of the unit operations are heaters which function in cooling or heating streams as they enter or leave reactors.

Despite most of the process units being relatively low energy consumers, the extraction unit (AS-REAC) stands out and requires significantly more energy supplied. This is a key unit, where the extraction of magnesium using ammonium sulphate is conducted at high temperatures (400 °C) in a gas-solid reaction. This is expected since the reaction to extract magnesium from the silicate mineral in this manner, is endothermic. Authors who have conducted energy analyses of this process have also identified this unit operation as the most intensive from an energy perspective (Nduagu et al., 2012a). The total amount of energy required for this unit for Scenario 1 is about 11 500 MJ/hr. The total required by the process in Scenario 2 is about 6 300 MJ/hr, meaning more than 80% of the process energy requirement is attributed to the extraction unit.

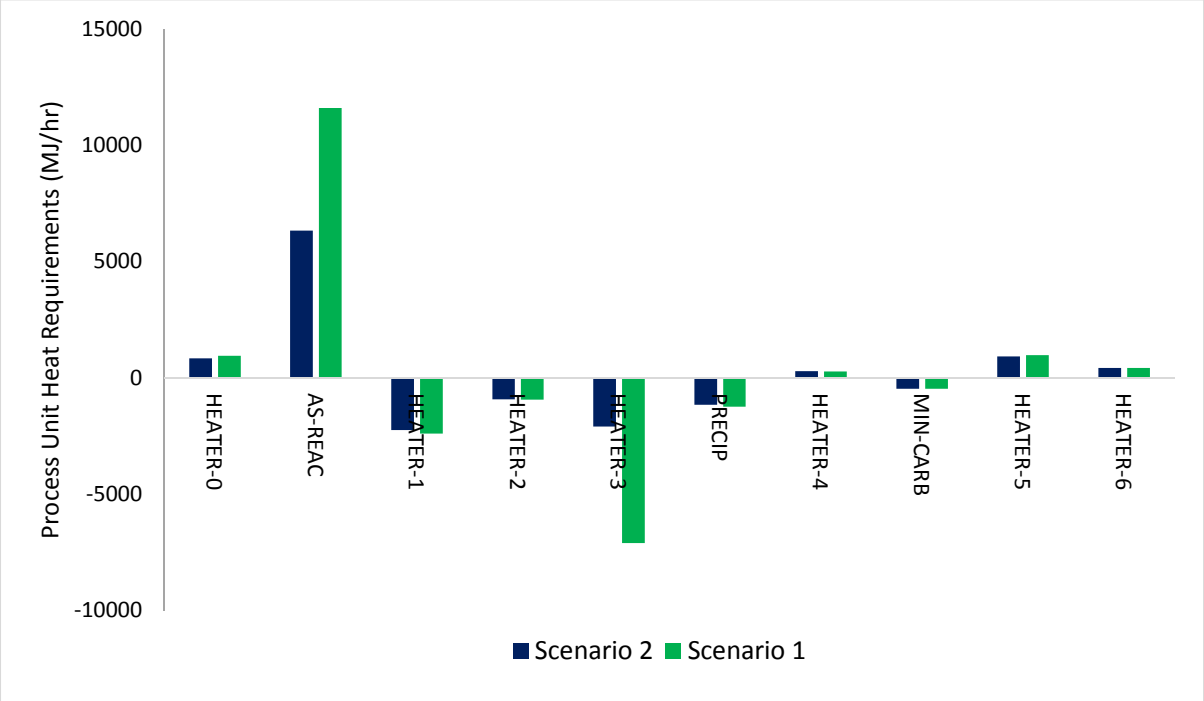


Figure 4-8: Energy requirements for major process units in the Åbo Akademi University process

It can be noted that the energy requirements of the majority of the process units are fairly unchanged with an increase in extraction and carbonation, aside from the extraction unit (AS-REAC) and the solids stream cooler (HEATER-3). This is due to the absence of the solids recycle stream (PYR-REC) in Scenario 2, where 100% of the pyroxene is converted to magnesium sulphate. As a result the solids product is just silicon dioxide, which is removed from the process. On the other hand at 66% extraction efficiency some unreacted pyroxene

(90%) is recycled. This recycle stream enters the reactor at lower temperatures than the reaction temperature thus requires additional heat to be brought up to the temperature at which the reaction occurs. This also explains the similarly marked difference in the energy released by the HEATER-3 process unit, which is the solids cooling unit.

4.3.3 Carbon Dioxide Footprint

Upon establishing material and energy demands of the process, carbon dioxide emissions associated with these demands can then be calculated. The contributions to the carbon dioxide footprint of process requirements are presented in Table 4-9 and Figure 4-9. The total footprints for the two scenarios (discussed in Section 4.3.1) are also presented.

Table 4-9: Process contributions to carbon dioxide footprint (kg-CO_2e)

Description	**Scenario 1**	**Scenario 2**
Ammonium Sulphate	232	232
Heat Requirements	1 019	634
Electricity Requirements	84	84
Water	6	6
CO_2 Released	13	24
Total Footprint	1 354	980

It can be noted that the total footprint in Scenario 1 is slightly above (1 354 kg-CO_2e) the threshold of 1 000 kg of carbon dioxide sequestered by the process whereas the footprint for Scenario 2 is slightly less than the threshold, in total (980 kg-CO_2e). This is indicates a relatively promising start for this process, from a carbon dioxide emissions view point. This is because it is envisioned that additional optimisation and heat integration could reduce the footprint further, as has been indicated in work conducted by Nduagu et al. (2012b). Nonetheless, in its current configuration the process is not sustainable for Scenario 1 (which is based on experimental work) and marginally sustainable for Scenario 2 (based on, unlikely, complete extraction) from a carbon dioxide emissions perspective.

Further analysis into individual carbon footprint contributions indicates that heat requirements are the most significant, accounting for at least 65% of the emissions resulting from this process. This finding is consistent with observations made by Nduagu et al. (2012b), who also found heat input to be the largest emissions contribution. In fact, the largest two contributors (heat and fresh ammonium sulphate) account for almost 90% of the footprint. This intimates efforts to reduce the carbon footprint should be primarily focused on these two areas.

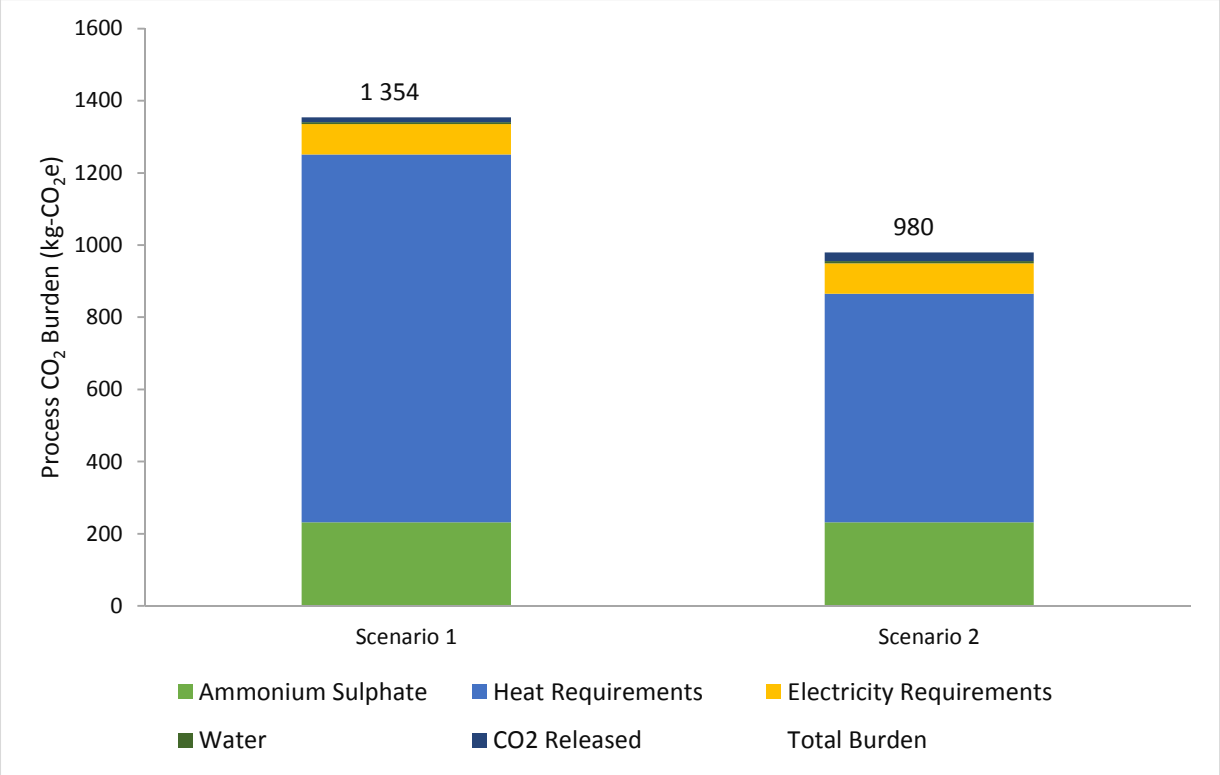


Figure 4-9: CO_2 footprint of material and energy requirements of Åbo Akademi University process (kg-CO_2e)

4.4 Mineral Acid pH-Swing Process

4.4.1 Flowsheet Description and Mass Balance

The mineral acid pH-swing process involves the extraction of magnesium from the silicate mineral (pyroxene) at low pH conditions, and the subsequent carbonation of the extracted cations at high pH or alkaline conditions. This process is based on the approach proposed by (Park et al., 2003) and experimental work conducted by (Vogeli, 2012; Meyer, 2014).

The simulation was run for three cases; based upon literature results (20% dissolution, 65% carbonation), a theoretical increase to 30% dissolution and 90% carbonation, and a theoretical 50% dissolution and 90% carbonation. These will be referred to as base case, Scenario 1 and Scenario 2, respectively, in subsequent discussions.

A material balance for the process for the base case is presented in Figure 4-10 indicating key flows within the process. A more detailed mass balance and flowsheet is provided in Appendix B and E respectively. Additionally, the key chemical reactions occurring in this process are presented in Table 4-10. It must be noted that in the case of this particular process these chemical reactions have been developed for simplicity (since none have been proposed) and may not represent the exact path and reactions occurring in reality.

Table 4-10: Key reactions occurring in the mineral acid pH-Swing process

Reactor Unit	Chemical Reaction	T (°C)	P (atm)
Mg-Extraction	$MgSiO_3+2HCl \rightarrow MgCl_2+SiO_2+H_2O$	70	1
pH Adjustment	$NaOH+HCl \rightarrow NaCl+H_2O$	25	1
Mineral Carbonation	$MgCl_2+H_2O+CO_2 \rightarrow MgCO_3+2HCl$	20	1

This process uses hydrochloric acid (HCl) to extract magnesium from pyroxene to produce 2 222 kg/hr of magnesium chloride in the dissolution reactor (MIN-DIS). These streams are both preheated to reaction conditions prior to being fed into the dissolution unit which operates at 70 °C. Alongside magnesium chloride, the product also carries unreacted pyroxene in a slurry. These streams are separated through a solid-liquid separation, and 80% of the solids stream is recycled back into the dissolution reactor, to improve the overall conversion of pyroxene from the 20% single pass conversion.

The leach solution is then sent through a pH adjustment (PH-ADJ) process. Here unreacted hydrochloric acid is reacted with excess (800 kg/hr) sodium hydroxide, to neutralize and adjust solution pH towards alkaline conditions. This is the step upon which the process is named, which provides the alkaline conditions that favour the carbonation reaction.

The pH adjusted leach solution (LEACH-2) is then fed to the mineral carbonation reactor (MIN-CARB) to react with 1 000 kg/hr of gaseous CO_2. The product of this reaction is 1 773 kg/hr of solid magnesium carbonate. This reaction has been assumed to also regenerate hydrochloric acid, which can then be used in the dissolution circuit. About 90% of the regenerated acid is recycled back to the dissolution circuit, with the balance considered to be spent acid and losses.

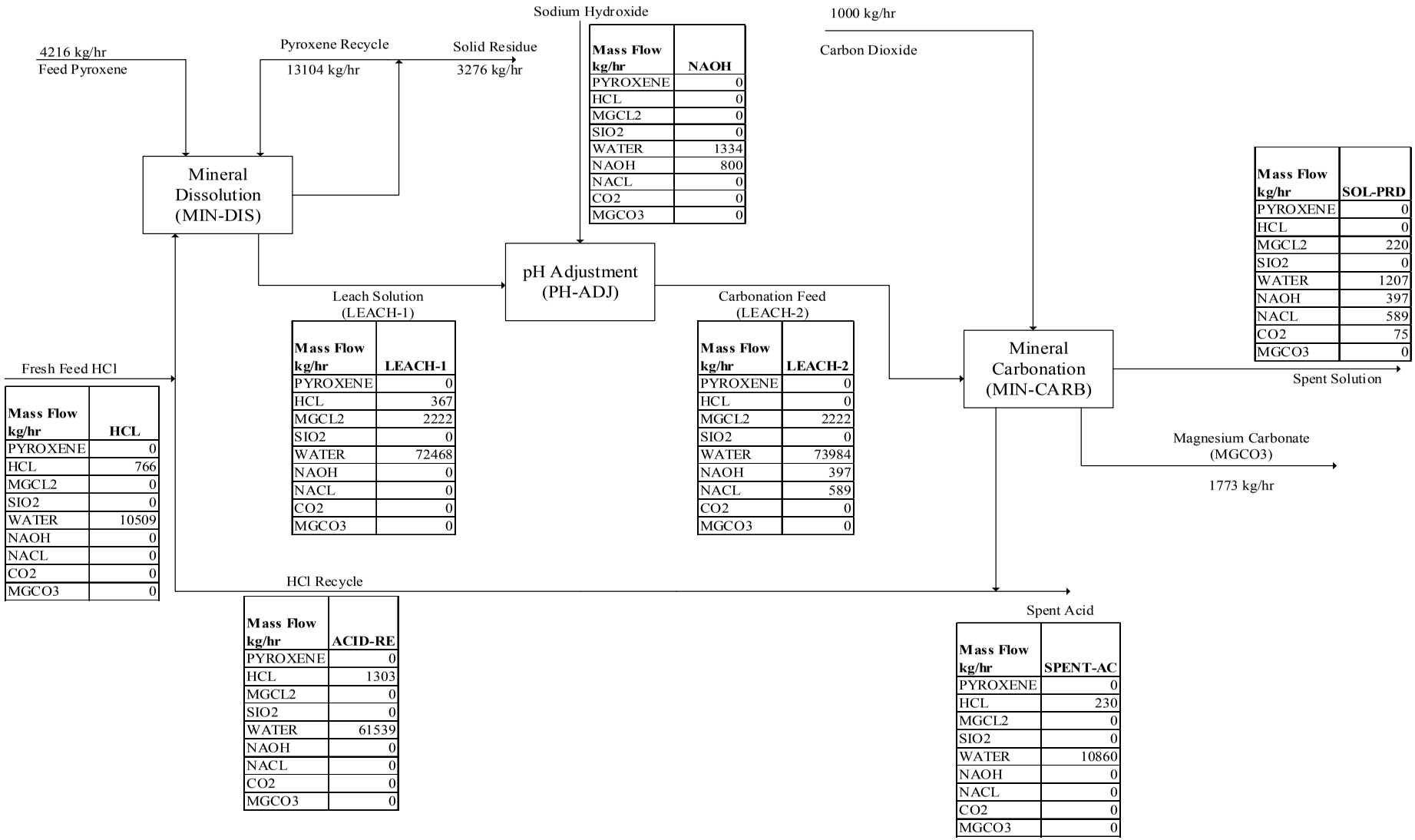


Figure 4-10: Material balance for mineral acid pH swing process for 20% extraction efficiency and 65% carbonation efficiency

The overall input streams to this process are presented in Table 4-11 as well as the quantities that are required for each case. The tons of feed pyroxene required to sequester a ton of carbon dioxide can deduced from Table 4-11 to be about 4.2, which is relatively high. This implies that larger size vessels would have to be designed to handle this material throughout the process. It can also be seen that the amount of hydrochloric acid and water required increasing from the base case to through to Scenario 2. This can be attributed to the increase in extraction efficiency, which at constant pyroxene input rate would require more acid to react with the silicate mineral. The use of an acid recycle stream substantially reduces external HCl requirement, which would be significantly higher since at least twice the moles of HCl are required to react with 1 mol of pyroxene, from a stoichiometry standpoint.

Table 4-11: Material requirements for mineral acid pH swing process

	Mass Flow (kg/hr)		
Component	Base Case	Scenario 1	Scenario 2
Carbon Dioxide	1 000	1 000	1 000
Pyroxene	4 216	4 216	4 216
Hydrochloric Acid	766	1 203	1 677
Sodium Hydroxide	800	800	800
Water	5 071	9 825	16 331

4.4.2 Process Energy Requirements

The energy requirements of major unit operations are presented in Figure 4-11. This figure indicates that the units HEATER-1, HEATER-2 and HEATER-3 require heat to be supplied. These units are, respectively, the preheaters for feed pyroxene, fresh feed hydrochloric acid and recycled acid being fed into the dissolution process. The acid recycle heater is the most demanding in terms of energy requirements, requiring up to 26 200 MJ/hr (Scenario 2). This constitutes more than 80% of the total energy requirements since up to 30 000 MJ/hr (Scenario 2) is required by the overall process.

It is worth noting that these requirements increase from the base case up to Scenario 2. This is a consequence of the increase in extraction efficiency which, as stated in Section 4.4.1, requires increased quantities of reagent. This is because across all simulations the recycle ratios were kept constant, thus any additional reagent would have to be sourced from an increased fresh feed input. This can be demonstrated by the observation that the percentage increase in fresh hydrochloric acid feed is comparable to the percentage increase in total energy requirements. For example, the percentage increase in hydrochloric acid from the base case to scenario 1 is

about 57% (from 766 kg/hr to 1203 kg/hr) which is comparable to the corresponding increase in energy, which is about 52% (from 14 760 MJ/hr to 22 380 MJ/hr).

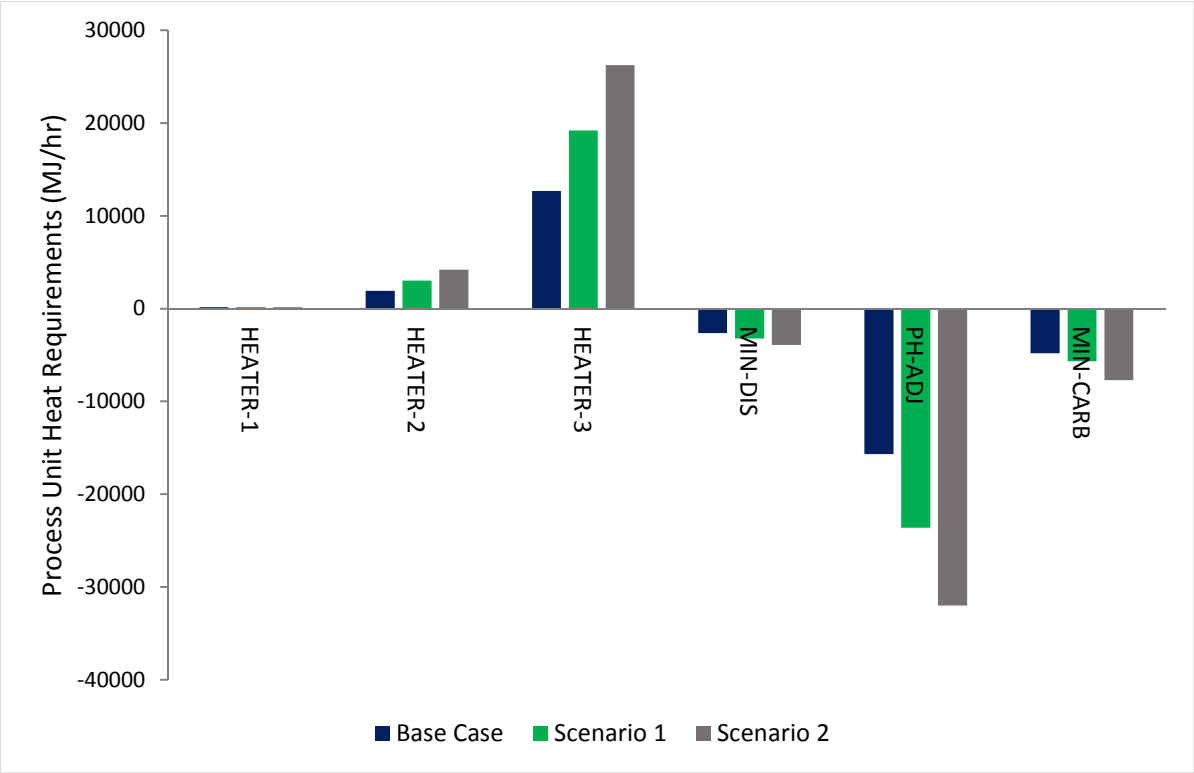


Figure 4-11: Energy requirements for major process units in the mineral acid pH swing process

It is also worth noting that there is an even split between energy releasing unit operations and those that require energy to be supplied. This could give an indication that heat integration may be worth exploring. In particular, the energy released during pH adjustment is comparable to the energy required by the acid recycle heater. However, to determine this additional analysis is required to establish the heat exchanger network that can be set up to achieve energy savings.

4.4.3 Carbon Dioxide Footprint

The material and energy requirements of the process ultimately translate to an environmental impact, in this case carbon dioxide equivalents, which is tabulated in Table 4-12 and presented in Figure 4-12. The contributions of process elements to the total carbon dioxide footprint of the process are indicated. Additionally, the impact of improvements in reaction efficiency on the carbon footprint is also demonstrated.

Table 4-12: Process contributions to carbon dioxide footprint (kg-CO_2e)

Description	Base Case	Scenario 1	Scenario 2
Compression	60	60	60
Heat	1 033	1 566	2 143
Hydrochloric Acid	1 004	1 577	2 198
Sodium Hydroxide	877	877	877
Water	77	116	159
CO2 Released	75	16	16
Total	3 126	4 214	5 454

The carbon footprint of all three cases considered for this process is above the threshold of 1 000 kg-CO_2e. The total footprint for this process varies from 3 126 kg-CO_2e to 5 454 kg-CO_2e from the base case to Scenario 2. This implies that this process appears unsustainable from a carbon dioxide emissions point of view in its current configuration.

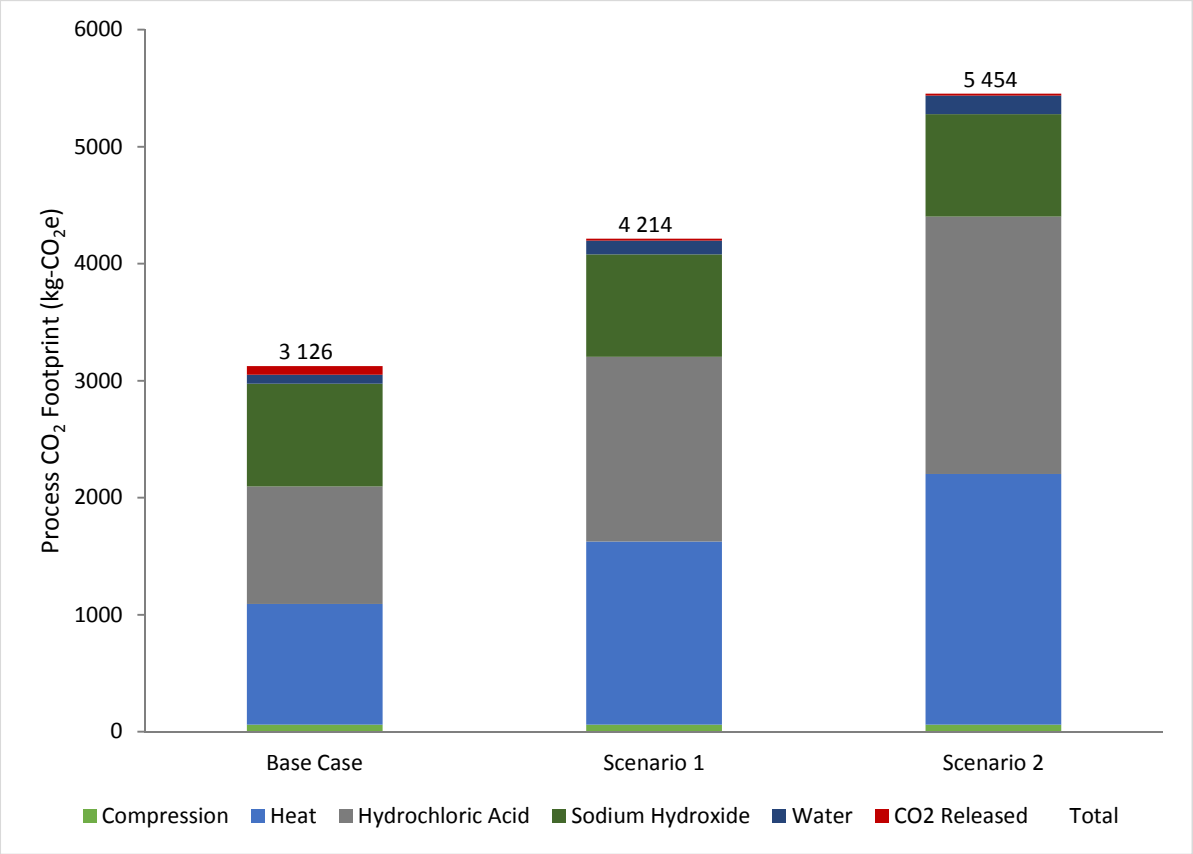


Figure 4-12: CO_2 footprint of material and energy requirements of mineral acid pH swing process (kg-CO_2e)

The major contributors to the footprint can be seen to be heat and fresh hydrochloric acid reagent requirements, with sodium hydroxide material requirements also contributing a significant portion to the carbon footprint. These account for between 77-89% of the footprint from the base case to Scenario 2. It is evident that these will have to be a focus for exploring

reductions in order to significantly lower the carbon footprint of the process, regardless of extent of conversion of the silicate mineral.

The high CO_2 footprint contribution for heat can be linked to the amount of heat required and the source through which this heat is obtained. Though the source, natural gas, has been identified as a cleaner fuel than coal or fuel oil, nonetheless the quantities required are substantial. Additionally, opportunities for energy integration appear to be limited. This represents a significant impediment to reduction of the contribution associated with heat generation, without exploring alternatives that are cleaner or using waste heat generated from other operations.

The carbon dioxide footprint associated with fresh hydrochloric acid is linked to the amount required as well as the means of production of the reagent. Incorporating recycle streams significantly reduces the amount of fresh acid required, from at least twice the amount of pyroxene to just above a third of the amount of pyroxene as discussed in Section 4.4.1. This may not be sufficient since the synthesis of hydrochloric acid results in about 1.3 kg-CO_2e for every kilogram of hydrochloric acid produced. Considering cleaner alternatives to the direct synthesis method may be useful.

Consistent with findings in the material and energy requirement results, the carbon dioxide footprint of the process increases from the base case through to Scenario 2, due to the explanation provided in Section 4.4.1. This is because for a constant emissions impact per unit requirement, the amount of material or energy required is directly proportional to the footprint accrued as a result of that requirement.

4.5 Direct Aqueous Carbonation Process

4.5.1 Flowsheet Description and Mass Balance

This is an aqueous carbonation process where the dissolution and carbonation steps occur in the same process step. It is considered the simplest approach, and makes use of carbonic acid produced through carbon dioxide dissolved in water as the extractive reagent. This process is based on work done at the National Energy Technology Laboratory (O'Connor et al., 2002; Gerdemann et al., 2007), though no work has been conducted with pyroxene as the silicate mineral feedstock.

The simulations for this process were run for the case where conversion was a modest 5%, as well as a relatively higher 20% conversion. These conversions were selected as pyroxene is relatively less reactive, and lower conversions would be expected for the carbonation of this

mineral than those provided in literature for serpentine and olivine, under industrial time-scales. The chemical reactions occurring in the process are given in Table 4-13. It is assumed that the first reaction proceeds to completion, thus the conversions referred to are for the conversion of the silicate mineral to magnesium carbonate.

Table 4-13: Chemical reactions occurring in the direct aqueous carbonation process

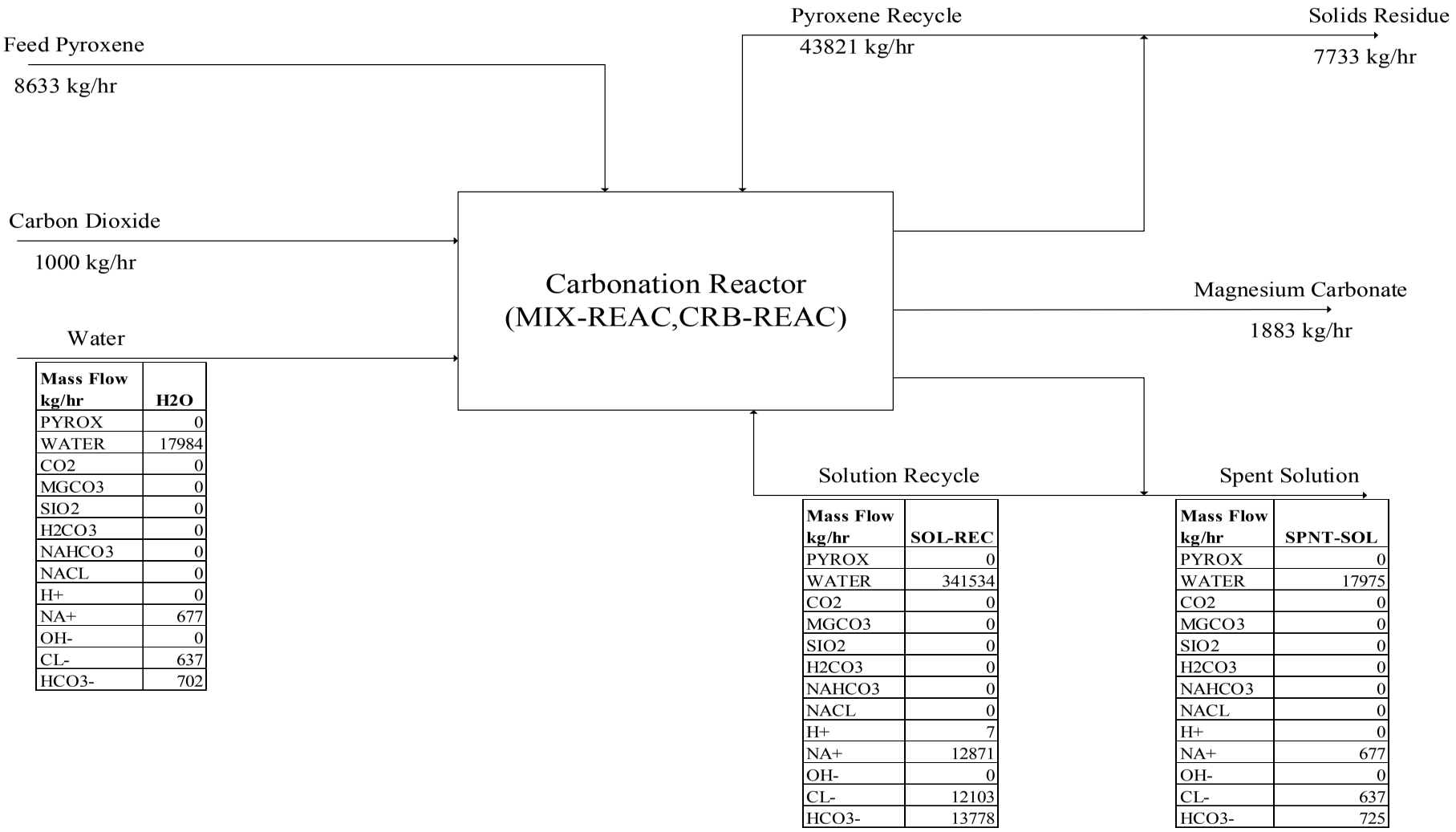
Reactor Unit	Chemical Reaction	T (°C)	P (atm)
Carbonation	$H_2O+CO_2 \rightarrow H_2CO_3$	185	150
	$MgSiO_3+H_2CO_3 \rightarrow MgCO_3+SiO_2+H_2O$	185	150

The material balance for the direct aqueous carbonation process (for the case where 5% carbonation is achieved) is presented in Figure 4-13. This shows the key flows within the process that sequesters 1 000 kg/hr of carbon dioxide. A more detailed Aspen Plus simulation diagram is presented in Appendix E, with the corresponding material balance tables provided in Appendix B.

The direct aqueous process has been found to be enhanced by the addition of sodium bicarbonate and sodium chloride (O'Connor et al., 2000), thus the water feed stream carries about 2 016 kg/hr of ions from these components. This component flowrate corresponds to 966 kg/hr sodium bicarbonate and 1 050 kg/hr sodium chloride mixed with the feed water. These amounts were determined based on the optimum compositions provided by Gerdemann et al. (2007), given in Table 2-3.

The water in this stream dissolves carbon dioxide producing carbonic acid, which facilitates the extraction of magnesium from pyroxene through the H+ proton. It is assumed that the carbon dioxide completely dissolves in water, since the large amounts of water resulting in a 15% solids slurry (O'Connor et al., 2005) used are assumed to result in a solution below the saturation point at the reaction conditions. The bicarbonate then carbonates the magnesium precipitating 1 883 kg/hr solid magnesium carbonate.

Due to the low single pass conversion in the process, a large 43 821 kg/hr recycle stream is used to feed back into the carbonation reactor, unreacted pyroxene. This improves the process' overall conversion. This stream represents 85% of the solids leaving the reactor. To increase reagent usage, a large amount of the solution is also recycled (95% of liquids) back into the carbonation reactor.



Mass Flow kg/hr	H2O
PYROX	0
WATER	17984
CO2	0
MGCO3	0
SIO2	0
H2CO3	0
NAHCO3	0
NACL	0
H+	0
NA+	677
OH-	0
CL-	637
HCO3-	702

Mass Flow kg/hr	SOL-REC
PYROX	0
WATER	341534
CO2	0
MGCO3	0
SIO2	0
H2CO3	0
NAHCO3	0
NACL	0
H+	7
NA+	12871
OH-	0
CL-	12103
HCO3-	13778

Mass Flow kg/hr	SPNT-SOL
PYROX	0
WATER	17975
CO2	0
MGCO3	0
SIO2	0
H2CO3	0
NAHCO3	0
NACL	0
H+	0
NA+	677
OH-	0
CL-	637
HCO3-	725

Figure 4-13: Material balance for direct aqueous carbonation process for 5% carbonation efficiency

The input material requirements of the process are presented in Table 4-14. These show that significant quantities of pyroxene would be required to sequester a ton of carbon dioxide using this process. The quantity of feed pyroxene required per ton of carbon dioxide sequestered varies considerably for the two cases for which simulations were conducted, from about 8.6 in the case of 5% conversion to 3.5 when conversion increases to 20%. The high value has implications that extend to influencing the size of units that will be required to process this material, as well as larger recycle streams.

Table 4-14: Material requirements for direct aqueous carbonation process

	Mass Flow (kg/hr)	
Component	5% Conversion	20% Conversion
Carbon Dioxide	1 000	1 000
Pyroxene	8 633	3 514
Water	17 984	7819
Sodium Bicarbonate	966	420
Sodium Chloride	1 050	468

4.5.2 Process Energy Requirements

The energy requirements for most unit operations are relatively lower than the most intensive unit (HEATER-3) as shown in Figure 4-14. These units release or consume less than 2 000 MJ/hr in comparison to about 12 500 MJ/hr required by HEATER-3. This unit is the feed water stream preheater that heats up water to 185 °C, the reaction conditions, prior to carbonation. This implies that even with 100% of the heat released by process units being used (which is improbable) it would be insufficient to supply the energy requirements for this unit. However, the use of the reactor exit stream to pre-heat the feed to the reactor could potentially significantly decrease this requirement, and has been suggested by some (Nduagu et al., 2012b; Giannoulakis et al., 2014).

The carbonation reactor was split into two reactor blocks (MIX-REAC, CRB-REAC) to separate the modelling of the dissolution of carbon dioxide in water and the carbonation reaction. This was done for computational simplicity during simulation development, since in reality these reactions occur in the same reactor. The formation of carbonic acid (MIX-REAC) and the carbonation reaction (CRB-REAC) are exothermic, however, release less than 2 000 MJ/hr combined. The production of carbonic acid was assumed to proceed to completion.

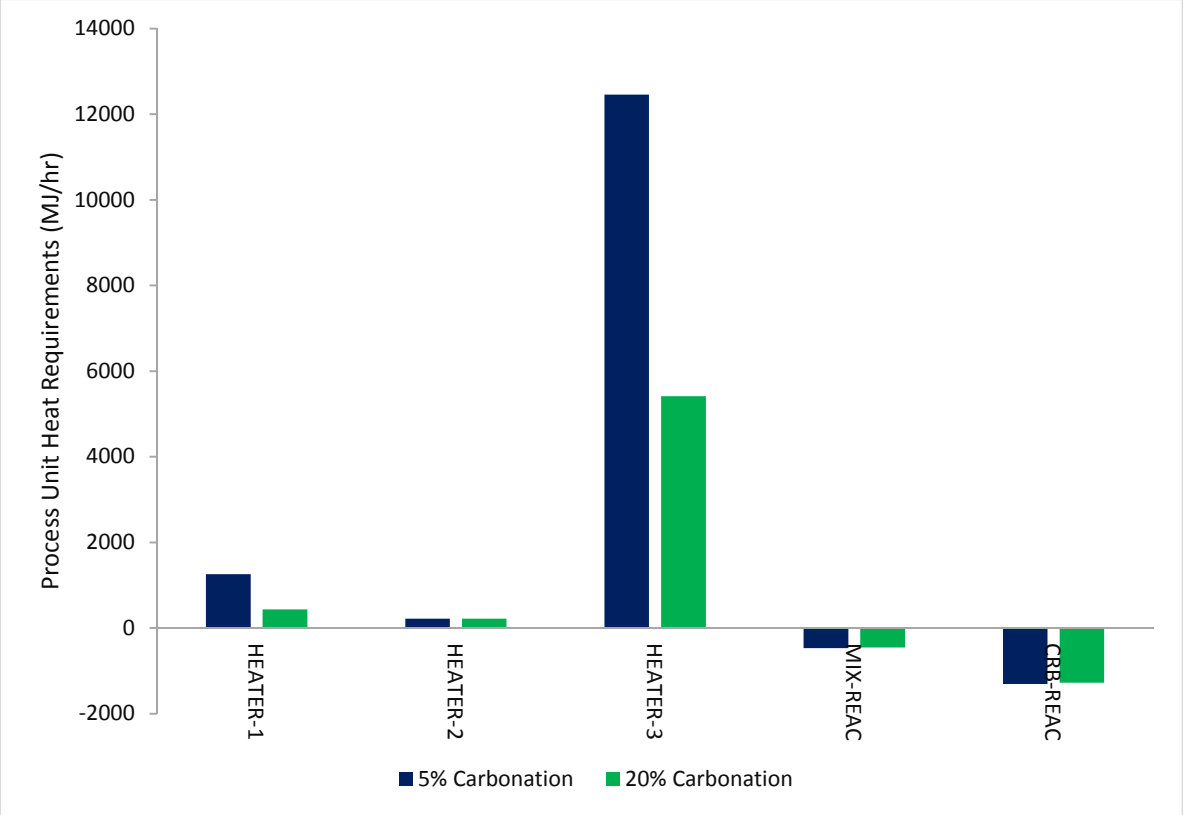


Figure 4-14: Energy requirements for major process units in the direct aqueous carbonation process

Figure 4-14 also shows that the energy requirement is fairly constant with an increase in conversion from 5% to 20%, with the exception of HEATER-1. The decrease in requirement in HEATER-1 is linked to the decrease in pyroxene feedstock that requires preheating, whereas the decrease in requirement for HEATER-3 is linked to the decrease in make-up aqueous reagent. The amount of carbon dioxide fed into the process does not change, hence HEATER-2 remains constant. This process also requires the compression of carbon dioxide to the reaction pressure of 150 atm. This compression requires 50 MJ/hr of electrical energy, which is significantly lower in absolute terms in comparison to heat requirements.

4.5.3 Carbon Dioxide Footprint

The carbon dioxide emissions impacts of various process requirements are presented in Figure 4-15 and Table 4-15. The total emissions resulting from summing up the individual contributions of process requirements are also provided. The carbon dioxide emissions for both carbonation efficiencies simulated are above 1 000 kg of CO_2 sequestered, at 2 364 kg-CO_2e for 5% carbonation and 1 095 kg-CO_2e for 20% carbonation. This suggests that the process cannot be considered sustainable from a carbon dioxide emissions perspective.

Table 4-15: Process contributions to carbon dioxide footprint (kg-CO_2e)

Description	5% Carbonation	20% Carbonation
Water	117	51
Heat Requirements	998	435
Electricity	115	115
Sodium Bicarbonate	1 016	442
Sodium Chloride	119	53
Total	2 364	1 095

These emissions are higher than those reported by Kichorfer et al. (2012) discussed in Section 2.2, albeit using different silicate minerals. However, it must be noted that the findings of those authors were based on general first-order level approximations of mass and energy requirements which could result in underestimation of the emissions contribution. In fact, the authors recommended the use of more rigorous and comprehensive modelling on simulation software like Aspen to better estimate reaction rates and energy requirements (Kirchofer et al., 2012). Additionally, the footprint associated with chemical reagent production was not included in accounting for emissions contributions.

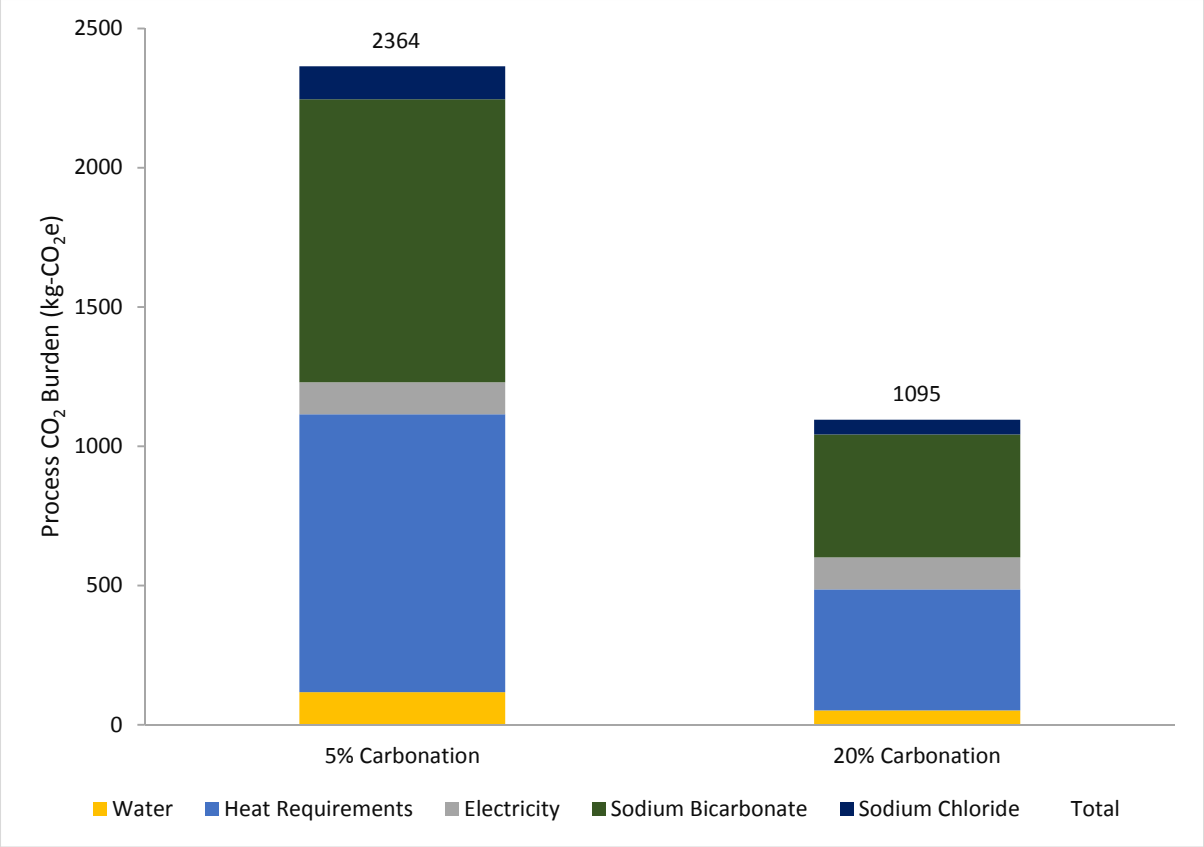


Figure 4-15: CO_2 footprint of material and energy requirements of direct aqueous carbonation process (kg-CO_2e)

The results indicate that an increase in the carbonation efficiency from 5% to 20% could potentially result in the halving of the carbon footprint of the direct aqueous process. This brings the process closer to carbon neutrality, without the consideration of process improvements such as heat integration.

The primary contributors to the carbon dioxide footprint are heat requirements and the production of fresh sodium bicarbonate feed. These two account for 90% of the total emissions impact of the direct aqueous carbonation process. In this regard, focus to reduce overall emissions of the process should be focused on reducing these contributions. It is also worth noting that individually, the production of heat contributes about 1000 kg-CO_2e, as well as the production of sodium bicarbonate. These, individually, push the process to the verge or just over carbon neutrality. This means that it is not enough to reduce one of these contributions in isolation, without achieving comparative reductions to the other.

Chapter 5

Discussion of Results

The selected mineral carbonation processes result in varied material and energy requirements, and consequently varied carbon dioxide footprints. This section analyses and compares the processes from an energy and carbon dioxide footprint point of view, on the basis of the study results (Chapter 4). Also discussed are the potential effects of factors and variables associated with the key assumptions of the study. These effects pertain to the performance and viability of the proposed processes for the industrial-scale mineral carbonation of pyroxene-based feedstock, from both a technical and carbon neutrality perspective.

5.1 Mineral Carbonation Process Energy Comparisons

5.1.1 General Comparisons

Figure 5-1 indicates the total heat required by the individual processes to sequester a ton of carbon dioxide. This discussion focusses on process heat since it accounts for the majority of process energy requirements, which include electricity and heat.

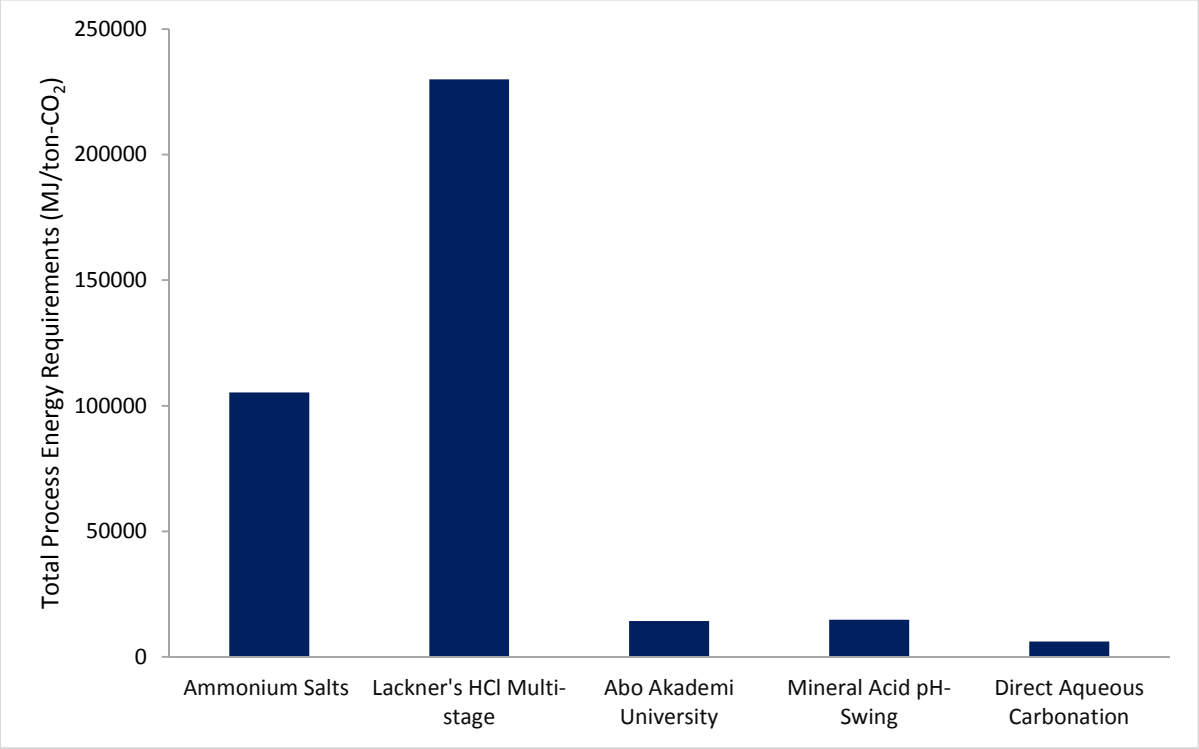


Figure 5-1: Comparison of process heat requirements of selected carbonation processes

The results presented are based on the base case scenarios for all the processes, that is, based on the literature conversions or the minimum estimate made in absence of literature data. Lackner's HCl multi-stage process has the highest heat requirements of all the proposed processes with total heat requirements of 230×10^3 MJ/ton-CO_2 sequestered. This is followed by the ammonium salts process which requires just under half the heat at around 100×10^3 MJ/ton-CO_2 sequestered. Comparatively, the last three processes require less than 30×10^3 MJ/ton-CO_2 sequestered in total heat requirements. The process that requires the least heat is the direct aqueous process.

In general, it can be noted (Figure 5-1) that, with the exception of the direct aqueous process the aqueous processes have higher heat requirements when compared to the gas-solid Åbo Akademi University process. This is despite the high temperatures used in this process, particularly in the extraction and carbonation stages which use temperatures as high as 450 °C and pressures up to 20 bar. This temperature is higher than even the highest temperatures used in the aqueous processes (300 °C for thermal decomposition in the ammonium salts process). This appears somewhat counterintuitive considering that the expectation would be that higher temperatures and pressures result in higher heat requirements. This is not the case for the mineral carbonation processes considered.

This trend can be attributed to the strong direct link between heat consumption and the quantity of water that is used in the process. The Åbo Akademi University process requires just 848 kg/hr of fresh feed water, whereas the aqueous processes generally require more than 10 000 kg/hr fresh feed water. Taking into account the recycle streams used in the selected processes, the water flows in the unit operations in the process are even larger than this feed input. With these large quantities of water requiring heating, the amount of heat required is increased substantially. Additionally, the evaporation of water in aqueous mineral carbonation processes is also a significant contributor to heat requirements. This involves a phase change which is accompanied by a latent heat of vaporisation that needs to be supplied, in addition to temperature-increasing heat, to convert the water into evaporated steam. It is thus not a coincidence that the two most intensive processes from a heat requirements perspective require the two largest water inputs (Table 5-1) and involve evaporation.

This observation is corroborated by work conducted by Dri et al. (2014), and noted by Sanna et al. (2014b), on the ammonium salts process, who noted that the heat associated with water evaporation in the ammonium salts process is excessive. In fact, in this process, the evaporation

of water has higher energy requirements than the thermal decomposition of ammonium sulphate to regenerate ammonium bisulphate and ammonia (see Figure 4-2 in Section 4.1.2 in Chapter 4) which occurs at a much higher temperature of 300 °C. Similar concerns have been raised regarding Lackner's multi-stage HCl approach (Newall et al., 2000; Olajire, 2013). These findings do not imply that temperature is not an important variable in mineral carbonation operations, only that they draw attention to possibility that the presence and quantity of water in the process can influence the energy requirements much more than operating temperatures. This highlights an important shortcoming of the aqueous carbonation processes, with the large quantities of water used also having a negative effect on the footprint associated with heating requirements, and hence, sustainability of these processes.

5.1.2 Comparisons between Aqueous Processes

Amongst the aqueous carbonation processes the most energy intensive process is Lackner's multistage HCl process, whereas the direct aqueous process is the least intensive (Table 5-1).

Table 5-1: Comparison between feed water and process energy requirements of indirect aqueous processes

Aqueous Carbonation Process	Fresh Water Feed (kg/hr)	Process Energy Requirements (MJ/hr)
Direct Aqueous	17 984	6 073
Lackner's Multi-Stage HCl	25 071	229 962
Ammonium Salts	12 839	105 349
Mineral Acid pH-Swing	11 843	14 760

Amongst the indirect aqueous processes, the link between the quantity of water and energy requirements is evident, with the process energy requirements increasing as the consumption of fresh water increases. Furthermore, the impact of phase change is also apparent in the much larger energy requirements of Lackner's multi-stage HCl process and the ammonium salts in comparison to the mineral acid pH swing process, which does not involve phase change. The However, the direct aqueous process, though using more water (18 000 kg/hr), uses less energy than the ammonium salts (13 000 kg/hr) and the mineral acid pH swing (12 000 kg/hr) indirect aqueous processes, as shown in Table 5-1. The comparison between direct aqueous and indirect aqueous processes appears to indicate another factor influencing the energy intensity of the aqueous carbonation routes, process simplicity. The direct aqueous process is a relatively simple process with one major reactor unit operating at a single temperature, whereas the indirect processes have multiple major reactor units operating at different temperatures, requiring intermediate heating which raises heat requirements.

These observations suggest that for aqueous mineral carbonation processes to reduce some of their energy requirements, it may be advisable to avoid energy intensive unit operations that involve phase changes such as evaporation, in addition to minimising water usage.

5.2 Mineral Carbonation Carbon Dioxide Footprint Comparisons

5.2.1 Comparisons of Overall CO_2 Footprints

A comparison of the carbon dioxide footprint of the selected mineral carbonation processes is presented in Figure 5-2, for the base case of all processes (as explained in Section 5.1.1). A tabulated version of this figure, providing more detail is presented in Appendix F:. These provide information on the total emissions impact of the process, as well as individual contributions of process elements to the footprint.

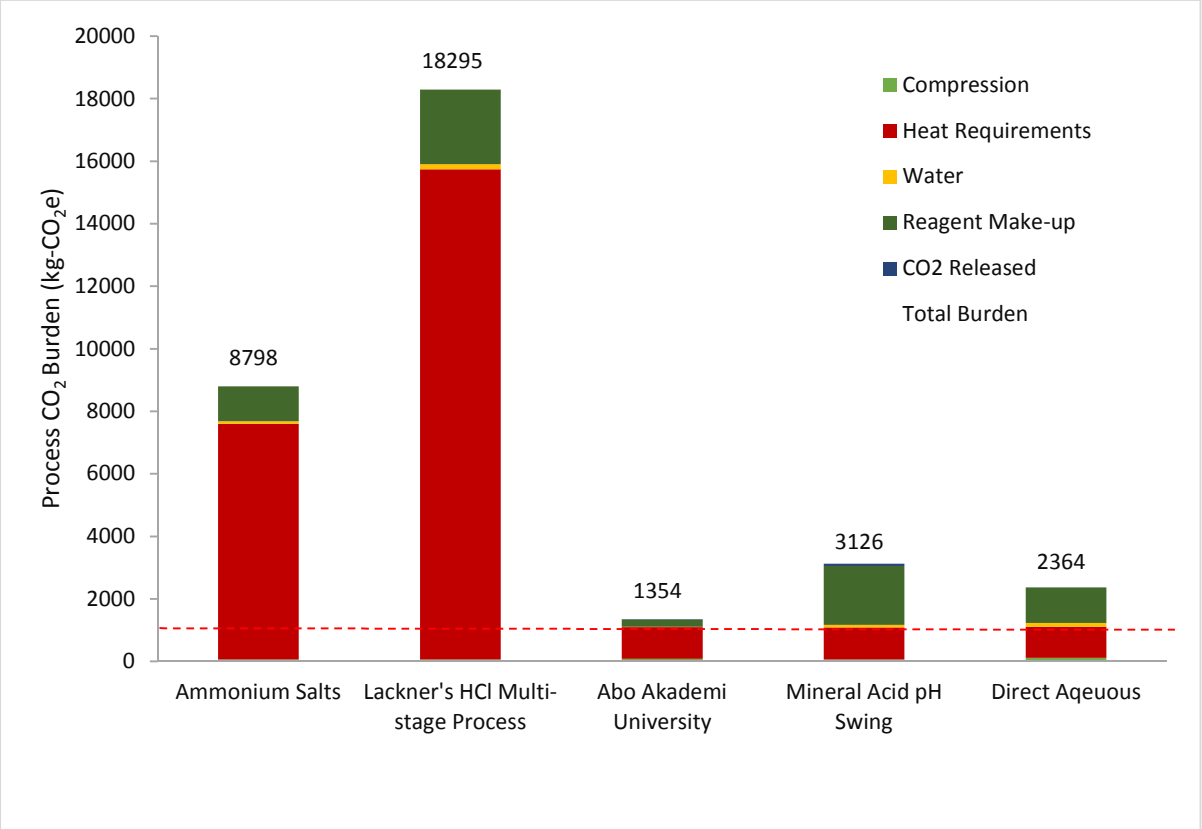


Figure 5-2: Comparison of carbon dioxide footprints of selected carbonation process system

The results in Figure 5-2 indicate that the mineral carbonation process having the highest carbon dioxide footprint is Lackner's multi-stage HCl process, followed by the ammonium salts process. This finding is consistent with the high heating requirements for these processes. The least emissions intensive process is the ÅAU process, followed by the direct aqueous process and the mineral acid pH swing process.

However, in terms of carbon neutrality, none of the process resulted in a net reduction in carbon dioxide emissions. This means that the amount of carbon dioxide emitted exceeds the amount sequestered, particularly in the cases of Lackner's multi-stage HCl process and the ammonium salts process. The processes were designed for the sequestration of 1 000 kg/hr of carbon dioxide, and the closest to achieving this target is the ÅAU process, with net emissions of 354 kg-CO_2e.

5.2.2 Process Contributions

Table 5-2 summarises the percentage contributions of the various processes to total carbon dioxide emissions.

Table 5-2: Percentage contributions of process requirements to total carbon dioxide emissions

Description	Ammonium Salts	Lackner's HCl Multi-stage Process	Abo Akademi University	Mineral Acid pH Swing	Direct Aqueous
Compression	1%	0%	6%	2%	5%
Heat Requirements	86%	86%	75%	33%	42%
Water	1%	1%	0%	2%	5%
Reagent Make-up	13%	13%	17%	60%	48%
CO_2 Released	0%	0%	1%	2%	0%

The results in Table 5-2 demonstrate that heat requirements and chemical reasgent make-up are the most emissions intensive processes involved in the mineral carbonation systems investigated. This appears to suggest that heat and chemical reagent requirements are a good predictor of process performance from a carbon emissions perspective, at least for the processes investigated in this study. Other process contributing to a minor extent are water supply and carbon dioxide compression. The effect of these processes on the overall carbon dioxide footprint are discussed in more detail in the sub-sections below.

Process Heat Requirements

For three of the five processes considered heat requirements are by far the largest emissions impact, accounting for up to 86% for Lackner's multi-stage HCl and the ammonium salts process as shown in Table 5-2. This percentage corresponds to a mammoth 15 677 kg-CO_2e in emissions. Even for the case where heat requirements are not the largest contributor (mineral acid pH swing and direct aqueous processes) they still account for a considerable share of the carbon footprint. This means that supply of heat requirements are an important consideration for the mineral carbonation process. This finding is consistent with observations made by a number of other authors and has been identified as one of the issues to resolved for mineral

carbonation to be successful in several state of the art reviews (Huijgen and Comans, 2003; Olajire, 2013; Sanna et al., 2014b).

Chemical Reagent Requirements

As can be seen in Figure 5-2, the second most (when not the first) carbon intensive process element for most of the mineral carbonation systems is reagent make-up. The reagents vary across the selected mineral carbonation processes, and include inorganic acids, ammonium salts, and inorganic salts such as sodium bicarbonate. For most processes (ammonium salts, Lackner's HCl multi-stage, direct aqueous, mineral acid pH swing) reagent production alone resulted in carbon dioxide emissions that exceed the amount sequestered, that is, resulted in the process being carbon positive (Table 5-3).

Table 5-3: Carbon dioxide emissions for chemical reagent make-up

Mineral Carbonation Process	Reagent Make-up Carbon Dioxide Footprint (kg-CO_2e)
Ammonium Salts	1 113
Lackner's HCl Multi-stage Process	2 394
Abo Akademi University	232
Mineral Acid pH Swing	1 881
Direct Aqueous	2 557

Studies in the literature have largely ignored the contribution of reagent make-up, or have been based on the assumption that 100% reagent recovery can be achieved (Nduagu et al., 2012b; Dri, 2014). This is unlikely to be the case in practice due to inevitable material losses in the process, as well as the need to purge in order to remove accumulating components. The potential impact of reagent make-up on the carbon dioxide emissions attributed to the mineral carbonation process highlights the importance of taking these contributions into account.

Water, Compression and CO_2 Released

Whilst the impact of water on process heat requirements was substantial (as discussed in Section 5.1), the carbon dioxide emissions associated with the supply of fresh water on carbon dioxide emissions is comparatively insignificant, particularly in the Åbo Akademi University process which uses relatively low quantities of feed water. In general, the emissions associated with the supply of water are less than 5% for all the selected mineral carbonation process systems (Table 5-2). The impact of compression of carbon dioxide on the total carbon dioxide footprint is also largely minimal, with the contribution not being more than 6% of the total emissions impact. As discussed earlier (Section 3.2.1), this included the compression for

transport by pipeline as well as any additional compression required to raise the pressure from the pipeline pressure for process purposes.

Another source of emissions that comes with some of the selected processes is the release of unreacted carbon dioxide. This is a factor for the Åbo Akademi University process as well as the mineral acid pH swing process, with the amount of carbon dioxide released accounting for 1% and 2% of the total emissions, respectively.

5.3 The Potential Viability of Selected Mineral Carbonation Processes

This section discusses general factors influencing the potential viability from both a technical and carbon neutrality perspective.

5.3.1 Process Technical Feasibility

It has been noted that pyroxene is stable, and sparingly reactive in comparison to other silicate minerals such as serpentine and olivine (Meyer et al., 2014; Sanna et al., 2014a) in terms of the extraction of magnesium cations from the silicate mineral matrix. This is a limiting step in the mineral carbonation of PGM tailings. Though all of the processes considered have been shown to be carbon positive, it important to consider the technical viability of the processes in the event that progress is made in future studies to make them sustainable in terms of resulting in a net reduction of carbon dioxide emissions.

The ammonium salts process is an integrated process based on the use of ammonium-based reagents for extraction, capture and carbonation. The extraction of magnesium from pyroxene has been demonstrated by Sanna et al. (2014a). The maximum extraction efficiencies achieved were a modest 30% in comparison to more than 90% for serpentine. Despite the low extraction efficiencies, it is foreseeable that this process could be implementable from a technical stand-point should improvements be made to its carbon neutrality. Numerous chemical processes operate at low single pass conversions, for example the production of ammonia via the Haber-Bosch process, but through the use of recycles are not only technically feasible, but economically profitable too. This leads to an assessment that from a technical perspective, the ammonium salts process could be feasible for the extraction of magnesium from pyroxene-rich PGM tailings and subsequent carbonation.

It has been mentioned that the mineral carbonation process proposed by Lackner et al. (1995) was based on theory only (Section 4.2). However, the extraction of magnesium from PGM tailings using hydrochloric acid has been demonstrated by Vogeli (2012). The author reported magnesium extraction efficiencies of up to 20% for the various samples considered. Through

a similar rationale made for the ammonium salts process, the process could be considered technically feasible and viable should improvements be implemented that move it towards carbon neutrality.

The Åbo Akademi University process is a gas-solid mineral carbonation that includes regeneration of chemical reagents through precipitation and evaporation. This process, though carbon positive, is one of the more promising from a carbon dioxide emissions point of view. However, the experiments conducted at the Åbo Akademi University have been focused on serpentine as the silicate mineral feedstock. Studies using pyroxene-based feedstock have not been conducted. Considering that the extraction efficiencies of the more reactive serpentine have been around 60-70%, without experimental work it is impossible to predict the extent, and even the possibility of reactivity of pyroxene-rich PGM tailings. Thus the technical feasibility of implementing this process is subject to experimental studies conducted to evaluate the possibility of extraction of magnesium from PGM tailings using this approach.

The mineral acid pH swing process has been developed from isolated experimental results obtained by Meyer (2014) and Vogeli (2012). It has not been developed into a complete carbonation process, and the chemistry has not been well defined. The authors reported an extraction efficiency of up to 20% using hydrochloric acid on PGM tailings. As mentioned earlier, with the use of recycle streams the overall conversion can be significantly improved in comparison to the relatively modest single pass conversion. However, the assumption that it is possible to recover and regenerate hydrochloric acid during the carbonation stage has not been validated experimentally, particularly at the low temperatures associated with the carbonation step. The technical feasibility of this process hinges on the feasibility of low temperature regeneration of the acid reagent, which has typically been achieved at higher temperatures (Lackner et al., 1995; Teir, 2008).

The direct aqueous process proposed and developed at the National Energy Technology Laboratory is a water-based extraction and carbonation single-step process. This process has been developed on the basis of experimental data for studies conducted on serpentine, olivine and wollastonite by the reseachers (O'Connor et al., 2005). The authors reported good conversions of more than 80% in some cases. Extraction and carbonation experiments using pyroxene or pyroxene-rich feedstock were not conducted by the authors. It is expected that pyroxene-rich PGM tailings, due to their stable nature, will be sparingly reactive under these conditions as Koukouzas et al. (2009) reported poor carbonation of harzburgite and pyroxenite

using this approach, under similar conditions. Additionally, under the mildly acidic conditions used by Meyer et al. (2014) the reported extraction efficiencies of magnesium were less than 5%, albeit at more moderate conditions compared to those used in the direct aqueous carbonation process. These low single pass conversions would require prohibitively large recycle loops to be implemented. Further empirical studies would thus need to be conducted in order to establish whether higher conversions can be achieved.

5.3.2 Heat Integration Potential

Heat integration has the potential to reduce external process heat demands, through the heat exchange of available heat between process streams. However, even with heat integration, not all available heat in process streams can be recovered due to thermodynamic constraints, as well as safety and process control considerations (Papoulias and Grossmann, 1983). The technique used for heat integration and heat exchanger network design is primarily pinch analysis. This has been reported to typically achieve energy savings of 20-30% (Linnhoff and Hindmarsh, 1983), although higher savings have been reported in some chemical processes (Kemp, 2007). Although limited studies have been conducted to rigorously evaluate the potential for heat integration in mineral carbonation processes, the benefit of heat integration was demonstrated through the work conducted by Nduagu et al. (2012b). These researchers were able to achieve a 35% reduction in the carbon dioxide footprint through heat integration, alongside systems expansion and mass allocation. A number of researchers have also suggested the use of reaction and exit stream heat for the pre-heating of the inlet stream in the direct aqueous process developed at the NETL (O'Connor et al., 2005; Nduagu et al., 2012b; Giannoulakis et al., 2014).

It should, however, be noted that in the case of Lackner's multi-stage HCl and ammonium salts processes heating requirements have to be reduced by more than 90%. This suggests that even with heat integration, the benefits in terms of making these processes sustainable from a carbon dioxide balance perspective are unlikely to be sufficient. On the other hand, the heat requirements for the direct aqueous process could be reduced through the use of the reactor exit stream to pre-heat the aqueous reagent feed stream, which is a major heat consumer, resulting in a potential reduction in external heat of about 70%. The reduction of the contribution to the footprint of heat requirements in the ÅAU process is also potentially feasible. The footprint associated with heat requirements for this process is just over 1 000 kg-CO_2e which, with a 30-50% reduction, could render this process a net carbon sink.

5.3.3 Additional Process Impacts and Plant Construction

The study did not include the energy consumption associated with pumping, separations and mixing, as it was assumed that this would to be much less than that associated with typically intensive unit operations such as heating and compression. Additionally, the impact of materials of construction, as well as energy associated with the actual construction of the mineral carbonation plant have not been considered. Inclusion of these factors can be expected to increase both the energy consumption and the total carbon dioxide emissions for the mineral carbonation process systems. The quantification of these emissions would need to be included in more detailed analyses of promising processes.

5.3.4 Chemical Reagent Recovery, Recycles and Losses

The recovery of chemical reagents, through the implementation of recycles streams in the flowsheet results in significantly less reagent make-up. However, due to the presence of some reaction products (such as silicon dioxide, that is recycled alongside reagent pyroxene), and excessive water in the recycle stream, that accumulate with recirculation, as well as requirements for excess feed into reactors, some reagent is lost as part of purges that remove these components, in order to avoid a build-up of these components, or excessively large recycle streams. The size of these purge streams varied generally between 10-15% of the splitter input stream, and was assumed to account for these losses, as well as losses associated with spent reagent and typical plant losses through for example leaks and evaporation. This loss is accounted for by the make-up reagent. In turn, the make-up reagent incurs a carbon footprint associated with its production. In this regard, there is an incentive to minimise the make-up reagent in order to reduce its impact on the carbon footprint. Reagent make-up accounts for a significant fraction of the carbon footprint, particularly in the case of the direct aqueous and mineral acid pH swing process (48% and 60% of the total carbon footprint, respectively). Furthermore, in four of the five selected processes (Lackner's multi-stage HCl, direct aqueous, ammonium salts, mineral acid pH swing) the carbon dioxide footprint contributions from the make-up of reagent exceeds the carbon dioxide sequestered by the process. It can be argued that the size of the recycle streams for the processes could be increased by adjusting the recycle ratio to reduce dependence on external reagent supply. However, increasing the recycle ratio may affect plant sizing, increase heat requirements, and also impact process stability as discussed in Chapter 4. In this regard, exploring optimal recycle ratios that balance these trade-offs to minimize the carbon footprint could be explored.

Chapter 6

Conclusions and Recommendations

6.1 Background and Motivation

Mineral carbonation has been identified as a potential carbon dioxide emissions reduction strategy. This process uses minerals, rich in magnesium or calcium, to permanently store gaseous carbon dioxide emissions in metal carbonate form. Several mineral carbonation process routes have been proposed ranging from direct gas-solid to indirect aqueous processes. The mineral carbonation process, though thermodynamically favourable, has been noted to be slow. As a result, a large body of work has been conducted to accelerate the carbonation process so that it may be justified for industrial implementation. These studies have been primarily focused on the more reactive and abundant silicate minerals such as serpentine and olivine. Consequently, proposed mineral carbonation processes have been developed on the basis of these minerals as feedstock. The acceleration of the carbonation process has also involved the use of chemical reagents, high temperatures and high pressures to enhance reaction kinetics. This has the potential to significantly increase the material and energy requirements of processes, and thus the carbon footprint. With limited comprehensive studies to evaluate the environmental implications of mineral carbonation, from a carbon neutrality perspective, a knowledge gap exists, particularly with regards to less reactive silicate mineral feedstock such as pyroxene-rich PGM tailings.

6.2 Research Objectives

South Africa has a large PGM industry that produces huge quantities of tailings that have been identified to have a potential for CO_2 sequestration. The over-arching objective of the study was to investigate the viability of using PGM tailings to sequester carbon dioxide on the basis of carbon neutrality. This study set out to achieve this by defining the following aims:

I. Identify potentially feasible flowsheets for the mineral carbonation of PGM tailings on the basis of literature.

II. Develop mass and energy balances for the identified processes using process simulation software.

III. Establish the carbon footprint of the process using Life Cycle Assessment (LCA) software.

6.3 Key Research Findings

This section summarises the key findings of the study presented in Chapters 2, 4 and 5.

6.3.1 Identification of Potentially Feasible Mineral Carbonation Processes

The first component of this study involved the identification of potentially feasible processes for the mineral carbonation of pyroxene-rich PGM tailings feedstock. This was achieved by conducting a detailed review and assessment of the available literature, in order to establish existing technologies and techniques that have been developed for mineral carbonation. The literature review demonstrated that several process routes exist for the mineral carbonation of silicate minerals, and that within these routes a considerable amount of research that has been done to understand and improve the performance of the processes. A general trend towards multi-stage processes such as in the gas-solid and pH swing processes was observed, whilst some researchers have continued developing single step process such as the direct aqueous process. The focus on accelerating process kinetics through temperature and pressure increases, as well as chemical reagent use by researchers was noted, as well as the development of processes with a focus on reagent regeneration. This was in contrast to the limited and under-developed studies that evaluate the effectiveness of the processes from a carbon balance or life-cycle assessment (LCA) perspective. Additionally, few of the processes have been developed beyond the laboratory scale. The brine solutions based SkyMine process is the only known commercial application to date.

On the basis of this survey, five processes were selected for further study: One multi-stage gas-solid process and four aqueous-based carbonation processes. These were:

1. Ammonium Salts Process – Indirect Aqueous pH Swing
2. Lackner's Multi-stage HCl Process – Indirect Aqueous Multi-stage
3. Åbo Akademi University (ÅAU) Process – Indirect Gas-Solid Multi-stage
4. Mineral Acid pH Swing Process – Indirect Aqueous pH Swing
5. Direct Aqueous Process – Direct Aqueous

6.3.2 Material and Energy Balance Simulations

The simulations of these processes were then developed, through the use of AspenPlus simulation software v8.0, for the purpose of establishing the flows of materials and energy within the selected mineral carbonation process systems. These were based on the sequestration

of 1 ton of carbon dioxide by pyroxene (as a proxy for PGM tailings). This served as a basis for carbon dioxide emissions accounting. The external material requirements of selected processes are vary since these processes make use of different chemical reagents, and operate at different reaction efficiencies.

Heat requirements were noted to account for the majority of energy requirements, hence were selected as the focus for further analysis. The process that required the most heat was Lackner's multi-stage process (230×10^3 MJ/ton-CO_2 sequestered), whereas the direct aqueous process required the least (6×10^3 MJ/ton-CO_2 sequestered). An analysis of heat requirements showed that aqueous processes generally required much more energy than the gas-solid ÅAU process, with the exception of the direct aqueous process. This was linked to the quantity of water used in the aqueous processes, which resulted in substantially higher energy requirements. This highlighted a short coming in the aqueous processes, that the benefits of process acceleration in aqueous media result in significant increases in heat requirements.

6.3.3 Mineral Carbonation Process Sustainability – Effectiveness to Sequester CO_2

The fundamental proposal of mineral carbonation is to be an effective carbon sink, that is, to reduce the overall carbon dioxide emissions released into the atmosphere. Consequently, the carbon dioxide balance is a good measure of the viability of a particular carbonation process. In this regard, the global warming potential (kg-CO_2e) of the process, which is a measure used to define greenhouse gas emissions in terms of a common unit related to the heat the greenhouse gas traps relative to carbon dioxide, was compared against the amount of carbon dioxide the process sequesters. The accounting of carbon dioxide emissions was conducted using SimaPro v7.7.3. background process modelling software. The carbon dioxide footprints for all selected processes were calculated and the carbon dioxide balance established. It was found that all selected processes were carbon positive, that is, ineffective as net carbon sinks.

The largest contributors to the overall emissions were primarily heat requirements and chemical reagent make-up. The two contributions were so large that they generally accounted for more than 85% of the total emissions of the selected processes, when combined. In the cases of the ammonium salts and Lackner's Multi-stage HCl processes this amounted to 98% and 99%, respectively. These were thus identified as key areas to focus efforts to reduce the overall emissions impact of mineral carbonation processes.

Lackner's multi-stage HCl process was found to be the have the highest carbon footprint, resulting in 18.2 tons of carbon dioxide emissions to sequester 1 ton of carbon dioxide. The second largest emitter was the ammonium salts process emitting eight times more CO_2 than it is intended to sequester. The mineral acid pH swing process resulted in three times more emissions than sequestered. The process with the least carbon dioxide footprint was the Åbo Akademi University (ÅAU) process, with just 354 kg-CO_2e of additional emissions. The direct aqueous process resulted in about 2 400 kg-CO_2e in emissions.

Generally, the aqueous mineral carbonation processes were considerably more emissions intensive than the gas-solid multi-stage ÅAU process. This was linked to the higher quantity of water used by the aqueous processes in comparison to the ÅAU process. It was observed that the large quantities of water used by these processes and changes of phase through evaporation substantially increase the energy requirements and thus the carbon dioxide footprint.

6.4 Recommendations

Although the selected processes were demonstrated to result in more carbon dioxide emissions than they sequester, the development of effective processes for the sequestration of carbon dioxide remains of key importance in terms of managing climate change. It is paramount that work in this strategic area is continued. However, it is evident that in some cases a lot of work still needs to be done to ensure that implemented mineral carbonation processes are reducing overall carbon dioxide emissions. In the case of mineral carbonation, it may be possible to reduce the carbon intensity of some of these processes sufficiently to render them net carbon negative. This is particularly the case for the three processes with the lowest carbon footprint: the mineral acid pH swing, the direct aqueous process, and more especially the Åbo Akademi University (ÅAU) process. It should, however, be noted that apart from limited preliminary experimental work on the mineral acid pH swing process, the technical feasibility of using pyroxene (the major component of PGM tailings) as feedstock for the processes has not been established to date. Preliminary testwork is thus recommended in the first instance to investigate the technical feasibility of using pyroxene as a feedstock for the direct aqueous and the ÅAU mineral carbonation processes.

In the second instance, further work needs to be conducted to reduce the carbon footprint on processes that are potentially feasible. This pertains in particular to the reduction of carbon

emissions associated with heating and the production of chemical reagents as feed to the process.

6.4.1 Reducing heating related carbon emissions

Process heat requirements have been identified as one of the two largest contributors to the emissions footprint of mineral carbonation processes. The two components of the emissions impact related to process heat requirements are the source of the heat, and the quantity of heat required. In this regard, the options for reducing emissions related to heat generation would be to either use an alternative heat source or to reduce the quantity of heat required, though the former would benefit all process cases.

The use of cleaner fuel sources for heat supply

The current source used to generate heat for the selected mineral carbonation processes is natural gas. This is considered the cleanest fossil fuel, and also the cheapest. However, it is still a fossil fuel and thus releases considerable amounts of carbon dioxide when burned. An alternative to consider may be the use of biomass as a source, which has been suggested to achieve near zero net emissions since the source (plants and other organic matter) absorbs carbon dioxide during its lifetime (European Climate Foundation, 2010). The European Climate Foundation (2010) suggests a reduction in carbon dioxide emissions of up to 98% by using biomass instead of fossil fuels. However, biomass has a low energy density at 8 GJ/t in comparison to natural gas at 56 GJ/t (McKendry, 2002) and is more expensive per MWh (European Climate Foundation, 2010).

The reduction of external heat supply

The reduction of the overall quantity of heat required is an equally, if not more, important lever in the reduction of emissions associated with heat generation. This can be accomplished through exploring heat integration opportunities, and using low temperature process operations.

Heat integration involves the recovery or reuse of process heat by matching process streams that require heat (cold streams) to those that carry heat (hot streams). This minimizes the external utility requirements of the process, and thus the emissions impact associated with the generation of utilities. The design of the heat exchanger system is typically conducted using techniques like Pinch Technology to match cold and hot streams effectively. The mineral carbonation processes could benefit from the exploration of heat integration and effective heat

exchanger network design. Hence, it is recommended that this be included in future work, so that the extent to which it can result to energy savings can be established.

The use of high temperatures to regenerate reagent, particularly in aqueous processes, results in a considerable footprint, from a carbon dioxide emissions perspective. Although processes that have integrated chemical reagent regeneration capabilities are attractive from a material use standpoint, it has been shown in this study that they can also incur huge energy penalties, primarily associated with regeneration. This highlights the importance of developing low temperature regeneration processes. Ideally, this would not just be limited to regeneration, but be the case for the entire process. The idea of using low temperature options has also been proposed by Sanna et al. (2014b), although few practical examples exist, particularly for reagents like ammonium bisulphate and hydrochloric acid. This suggests that additional work should be done in the mineral carbonation field, in general, to develop regeneration operations for promising processes that use more moderate temperatures. Otherwise, a re-evaluation of the balance between the costs and benefits of regeneration will have to be considered.

6.4.2 Reducing material and chemical related carbon emissions

The mineral carbonation process in its simplest form would be a direct gas-solid reaction between the silicate mineral and carbon dioxide. However, the kinetics of this reaction are too slow to be justifiable for industrial operation. This necessitates the use of chemical reagents to accelerate the carbonation process. This typically involves the use of acids, such as hydrochloric acid and ammonium salts for extraction, as well as bases such as ammonium and sodium hydroxide, and salts such as sodium chloride and sodium bicarbonate.

The use of chemical reagents has been identified as one of the major contributors in terms of carbon footprint for selected mineral carbonation processes. This emissions contribution is a function of the reagent production processes as well as the required quantities of reagent. This implies that these are the two levers of control for carbon dioxide emissions associated with chemical reagent use in the carbonation process.

The use of cleaner input materials

In most cases, the production of chemical reagents used in the mineral carbonation process involves energy intensive operations. For example, the production of hydrochloric acid using the direct synthesis approach is an energy intensive operation since a 2 000 °C burner is used to facilitate the burning of chlorine in hydrogen (Austin and Glowacki, 2005). Considering other less energy intensive production processes such as the Mannheim process, or sourcing it

as a by-product of other chemical processes such as the chlorination process could potentially reduce this emissions contribution. In this regard, using chemical reagent that are produced by cleaner processes in terms of carbon emissions is important for the reduction of this contribution. Additionally, exploring alternative reagents to achieve the same function in the process could also be useful in reducing the emissions contribution of chemical reagent make-up.

The reduction of make-up reagent consumption

The quantities of chemical reagent used in the process also affects the carbon emissions impact associated with external reagent production. The chemical reagents required vary from about 2.0 kg/kg-CO_2 for Lackner's multi-stage HCl process to as low as 0.4 kg/kg-CO_2 for the ÅAU process. A reduction in the amount of make-up reagent could be effected by either increasing recycle ratios or improving reaction efficiencies by altering process conditions. However, it must be noted this may affect process performance from a technical perspective, and also from an energy point of view.

6.5 Concluding Remarks

This thesis has highlighted the importance of adopting a holistic life cycle based approach to the evaluation of the performance of mineral carbonation processes. It has shown that enhancing process kinetics in isolation could result in processes that, whilst technically justifiable, may result in a net release of carbon dioxide emissions, further exacerbating the problem of global warming. However, mineral carbonation is an important carbon dioxide emissions reduction technology that should not be abandoned, considering the concerns with geological and ocean storage. It promises a permanent and safe option for the storage of carbon dioxide emissions, which could also make use of mineral industry waste streams. This has the potential to both reduce environmental impacts and enhance natural resource efficiency, through the improved utilisation of mined mineral material. However, it is clear that the technology is far from being a fully developed carbon dioxide emissions mitigation strategy. In particular, this study has identified a reduction in emissions associated with heating and production of chemical reagents as two key areas requiring attention. These emissions will need to be reduced substantially in most of the processes investigated, including the Lackner's multi-stage, ammonium salts, direct aqueous, and mineral acid pH swing processes. Developing low-temperature process operations, particularly for reagent regeneration, and optimising materials and energy use, whilst maintaining process kinetics performance, is the key to unlocking the potential of this technology. This is particularly important in the context

of PGM tailings, which is a less reactive feedstock, but offers the potential for recovery of additional PGM mineral value, which would improve the economics of potential processes. This will require not just a modification of existing processes, but also a shift in the underlying process design philosophy towards a holistic approach, that takes into account kinetic performance and environmental performance, with the next frontier being the improvement of the economics of the technology.

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Appendix A: Initialization Data for AspenPlus Simulations

A.1 Ammonium Salts Process

Table A-1: Initialization data for Aspen modelling of ammonium salts process

Block ID	Aspen Model	Property Method	Purpose	Input Specifications
HEATER-1	Heater	ELECNRTL	Preheats the feed stream of mineral prior to leaching.	Flash Type: Temperature-Pressure Temperature: 90 °C Pressure: 1 atm
HEATER-2	Heater	ELECNRTL	Preheats the feed stream of ammonium bisulphate prior to leaching.	Flash Type: Temperature-Pressure Temperature: 90 °C Pressure: 1 atm
SIO2-SEP	Sep	GLOBAL	Separates aqueous solution from silica and tailings residue.	Outlet Stream: SIO2-PYR Split Fraction: PYROXENE = 1 SIO2 = 1
MIN-DIS	RStoich	ELECNRTL	The ammonium salts-based extraction of magnesium from pyroxene to produce magnesium chloride.	Flash Type: Temperature-Pressure Temperature: 90 °C Pressure: 1 atm Reactions: Conversion = 30%, 50%, 90% $MgSiO_3+2NH_4^+ +2HSO_4^- \rightarrow MgSO_4+SiO_2+(NH_4)_2SO_4+H_2O$
HEATER-3	Heater	ELECNRTL	Cools LEACH-1 stream to PH-ADJ reaction temperature.	Flash Type: Temperature-Pressure Temperature: 25 °C Pressure: 1 atm
PH-ADJ	RStoich	ELECNRTL	Adjust solution pH from acidic to alkaline conditions.	Flash Type: Temperature-Pressure Temperature: 25 °C Pressure: 1 atm Reactions: $NH_4^+ +HSO_4^- +NH_4OH \rightarrow (NH_4)_2SO_4+H_2O$
HEATER-4	Heater	ELECNRTL	Preheats pH adjusted leach solution to carbonation reaction conditions.	Flash Type: Temperature-Pressure Temperature: 80 °C Pressure: 1 atm
HEATER-5	Heater	ELECNRTL	Preheats ammonium bicarbonate stream to carbonation reaction conditions.	Flash Type: Temperature-Pressure Temperature: 80 °C Pressure: 1 atm

MIN-CARB	RStoich	ELECNRTL	The stable carbonate compound is produced from magnesium sulphate.	Flash Type: Temperature-Pressure Temperature: 80 °C Pressure: 1 atm Reactions: Conversion = 90% (All Cases) $Mg^{2+}+SO_4^{2-}+2NH_4^+ +2HCO_3^- +2H_2O \rightarrow MgCO_3+(NH_4)_2SO_4+CO_2$
CARB-SEP	Sep	GLOBAL	Separates out stable carbonate compound from sulphate-rich solution	Outlet Stream: MGCO3 Split Fraction: MGCO3 = 1
CO2-VENT	Sep	GLOBAL	Removes CO_2 from sulphate-rich solution.	Outlet Stream: CO2 Split Fraction: CO2= 1
HEATER-7	Heater	ELECNRTL	Cools CO_2 stream to capture conditions.	Flash Type: Temperature-Pressure Temperature: 10 °C Pressure: 1 atm
HEATER-9	Heater	ELECNRTL	Heats up sulphate-rich solution to evaporate water.	Flash Type: Temperature-Pressure Temperature: 120 °C Pressure: 1 atm
SEP-01	Sep	GLOBAL	Removes evaporated water from sulphate-rich stream.	Outlet Stream: EVAP-PRD Split Fraction: WATER = 0.99
HEATER-X	Heater	ELECNRTL	Preheats sulphate-rich stream to thermal decomposition reaction conditions.	Flash Type: Temperature-Pressure Temperature: 300 °C Pressure: 1 atm
EVAP	RStoich	ELECNRTL	Converts ammonium sulphate to ammonium bisulphate and ammonia via thermal decomposition.	Flash Type: Temperature-Pressure Temperature: 300 °C Pressure: 1 atm Reactions: $(NH_4)_2SO_4 \rightarrow NH_4HSO_4+NH_3$
HEATER-8	Heater	ELECNRTL	Cools evaporated steam prior to carbon capture.	Flash Type: Temperature-Pressure Temperature: 10 °C Pressure: 1 atm
HEATER-6	Heater	ELECNRTL	Cools decomposition product stream DEC-PRD.	Flash Type: Temperature-Pressure Temperature: 90 °C Pressure: 1 atm
SEP-02	Sep	GLOBAL	Separates ammonia from ammonium bisulphate.	Outlet Stream: CAP-NH3 Split Fraction: NH3 = 1
CO2-CAPT	RStoich	ELECNRTL	Captures CO_2 from producing ammonium bicarbonate.	Flash Type: Temperature-Pressure Temperature: 10 °C Pressure: 1 atm

				Reactions: $CO_2+H_2O+NH_3 \rightarrow NH_4HCO_3$
H2O-SEP	Sep	Global	Separates ammonium bicarbonate used in carbonation.	Outlet Stream: NH3 Split Fraction: WATER = 0.792 NH4HCO3 = 0
SPLIT-01	Fsplit	GLOBAL	Provides water for use in CO_2 capture.	Stream: CAP-H2O Split Fraction: 0.3
SPLIT-2	Fsplit	GLOBAL	Recycles unreacted pyroxene to dissolution reactor.	Stream: SIO2-PRD Split Fraction: 0.2
REC-SPLT	Fsplit	GLOBAL	Recycles regenerated acid to dissolution reactor.	Stream: BIS-PRD Split Fraction: 0.2
MIX-1	Mixer	ELECNRTL	Produces solution.	Pressure: 1 atm Valid Phases: Vapor-Liquid

A.2 Lackner's Multi-stage HCl (AAU) Process

Table A-2: Initialization data for Aspen Modelling of Lackner's multi-stage process

Block ID	**Aspen Model**	**Property Method**	**Purpose**	**Input Specifications**
HEATER-1	Heater	ELECNRTL	Preheats the feed stream of mineral prior to leaching.	Flash Type: Temperature-Pressure Temperature: 70 °C Pressure: 1 atm
HEATER-2	Heater	ELECNRTL	Preheats the feed stream of hydrochloric acid prior to leaching.	Flash Type: Temperature-Pressure Temperature: 70 °C Pressure: 1 atm
MIN-DIS	RStoich	ELECNRTL	The acid-based extraction of magnesium from pyroxene to produce magnesium chloride.	Flash Type: Temperature-Pressure Temperature: 70 °C Pressure: 1 atm Reactions: $MgSiO_3+2H^+ +2Cl^- +5H_2O \rightarrow MgCl_2 \cdot 6H_2O+SiO_2$
SPLIT-1	Fsplit	GLOBAL	Recycles unreacted pyroxene to dissolution reactor.	Stream: PYR-REC Split Fraction: 0.9

SEP-1	Sep	GLOBAL	Separates aqueous magnesium chloride from silica and tailings residue.	Outlet Stream: PYR-SIO2 Split Fraction: PYROXENE = 1 SIO2 = 1
CONV	RStoich	ELECNRTL	Magnesium chloride conversion and regeneration of hydrochloric acid.	Flash Type: Temperature-Pressure Temperature: 150 °C Pressure: 1 atm Reactions: $MgCl_2 \cdot 6H_2O \rightarrow MgOHCl + HCl + 5H_2O$
SEP-5	Sep	GLOBAL	Removes regenerated acid from product stream.	Outlet Stream: ACID Split Fraction: HCL= 1 WATER = 0.8
HEATER-4	Heater	ELECNRTL	Cools and condenses regenerated acid stream.	Flash Type: Temperature-Pressure Temperature: 70 °C Pressure: 1 atm
REPART	RStoich	ELECNRTL	Reforms magnesium chloride hydroxide, producing magnesium hydroxide.	Flash Type: Temperature-Pressure Temperature: 25 °C Pressure: 1 atm Reactions: $2MgOHCl \rightarrow Mg(OH)_2 + MgCl_2$
SPLIT-2	Fsplit	GLOBAL	Recycles hydrochloric acid to the dissolution unit.	Stream: HCL-REC Split Fraction: 0.9
SEP-2	Sep	GLOBAL	Removes solid magnesium hydroxide from magnesium chloride solution	Outlet Stream: H2O-2 Split Fraction: MGCL2= 1 WATER = 1
MIN-CARB	RStoich	UNIQUAC	The stable carbonate compound is produced from magnesium hydroxide.	Flash Type: Temperature-Pressure Temperature: 680 K Pressure: 1 atm Reactions: $Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$
SEP-3	Sep	GLOBAL	Removes water from solid magnesium carbonate product.	Outlet Stream: H2O Split Fraction: WATER = 1

A.3 Åbo Akademi University (AAU) Process

Table A-3: Initialization data for Aspen Modelling of Åbo Akademi University process

Block ID	Aspen Model	Property Method	Purpose	Input Specifications
HEATER-0	Heater	UNIQUAC	Preheats pyroxene feed stream of mineral prior to leaching.	Flash Type: Temperature-Pressure Temperature: 400 °C Pressure: 1 atm
AS-REAC	RStoich	UNIQUAC	The ammonium sulphate-based extraction of magnesium from pyroxene to produce magnesium sulphate.	Flash Type: Temperature-Pressure Temperature: 400 °C Pressure: 1 atm Reactions: $MgSiO_3+(NH_4)_2SO_4 \rightarrow MgSO_4+SiO_2+2NH_3+H_2O$
SEP-1	Sep	GLOBAL	Separates gaseous ammonia and steam from solid products.	Outlet Stream: NH3-H2O Split Fraction: NH3 = 1 WATER = 1
HEATER-1	Heater	ELECNRTL	Condenses ammonia and water prior to precipitation.	Flash Type: Temperature-Pressure Temperature: 25 °C Pressure: 1 atm
HEATER-3	Heater	UNIQUAC	Cools solids stream prior to mixing with water.	Flash Type: Temperature-Pressure Temperature: 40 °C Pressure: 1 atm
MIXER-1	MIXER	ELECNRTL	Mixes solids stream with water, dissolving magnesium sulphate.	Pressure: 1 atm Valid-Phases: Vapor-Liquid
SEP-2	Sep	GLOBAL	Removes dissolved magnesium sulphate solution.	Outlet Stream: MGSO-4 Split Fraction: SULPHATE = 1 MGSO4 = 1 NH3 = 1 WATER = 1
PRECIP	RStoich	ELECNRTL	Precipitates magnesium hydroxide through reaction of ammonia, water and magnesium sulphate.	Flash Type: Temperature-Pressure Temperature: 40 °C Pressure: 1 atm Reactions: $Mg^{2+}+2NH_3+2H_2O+SO_4^{2-} \rightarrow Mg(OH)_2+(NH_4)_2SO_4$

SPLIT-3	FSplit	GLOBAL	Recycles pyroxene into the extraction unit.	Stream: PYR-REC Split Fraction: 0.9
SEP-3	Sep	GLOBAL	Separates magnesium hydroxide from sulphate stream.	Outlet Stream: SULF-REC Split Fraction: SULFATE = 1 WATER = 1
HEATER-4	Heater	ELECNRTL	Evaporates water from ammonium sulphate stream.	Flash Type: Temperature-Pressure Temperature: 110 °C Pressure: 1 atm
HEATER-5	Heater	UNIQUAC	Preheats magnesium hydroxide stream prior to carbonation.	Flash Type: Temperature-Pressure Temperature: 450 °C Pressure: 1 atm
HEATER-6	Heater	UNIQUAC	Preheats carbon dioxide stream prior to carbonation.	Flash Type: Temperature-Pressure Temperature: 450 °C Pressure: 20 bar
MIN-CARB	RStoich	UNIQUAC	Production of stable carbonate compound from magnesium hydroxide and carbon dioxide.	Flash Type: Temperature-Pressure Temperature: 450 °C Pressure: 20 bar Reactions: $Mg(OH)_2+CO_2 \rightarrow MgCO_3+H_2O$
SEP-4	Sep	GLOBAL	Removes stable carbonate stream.	Outlet Stream: CARB-STR Split Fraction: MGOH = 1 WATER = 1 CO2 = 1
SPLIT-1	FSplit	GLOBAL	Recycles unreacted components to carbonation reactor.	Outlet Stream: CARB-H2O Split Fraction: 0.9
HEATER-2	Heater	UNIQUAC	Cools product carbonate stream.	Flash Type: Temperature-Pressure Temperature: 30 °C Pressure: 20 bar
SEP-6	Sep	GLOBAL	Recycles unreacted components to carbonation reactor.	Outlet Stream: CARB-REC Split Fraction: MGOH = 1 CO2 = 1
SEP-5	Sep	GLOBAL	Separates steam from solid ammonium sulphate stream.	Outlet Stream: STEAM Split Fraction: WATER = 1
SPLIT-2	FSplit	GLOBAL	Recycles regenerated ammonium sulphate to extraction unit.	Outlet Stream: AS-REC Split Fraction: 0.9

A.4 Mineral Acid pH-Swing Process

Table A-4: Initialisation data for Aspen model of mineral acid pH swing process

Block ID	Aspen Model	Property Method	Purpose	Input Specifications
HEATER-1	Heater	ELECNRTL	Preheats the feed stream of mineral prior to leaching.	Flash Type: Temperature-Pressure Temperature: 70 °C Pressure: 1 atm
HEATER-2	Heater	ELECNRTL	Preheats the feed stream of hydrochloric acid prior to leaching.	Flash Type: Temperature-Pressure Temperature: 70 °C Pressure: 1 atm
HEATER-3	Heater	ELECNRTL	Heats acid recycle stream to reaction temperature.	Flash Type: Temperature-Pressure Temperature: 70 °C Pressure: 1 atm
MIN-DIS	RStoich	ELECNRTL	The acid-based extraction of magnesium from pyroxene to produce magnesium chloride.	Flash Type: Temperature-Pressure Temperature: 70 °C Pressure: 1 atm Reactions: $MgSiO_3+2H^++2Cl^-\rightarrow MgCl_2+SiO_2+H_2O$
SEP-1	Sep	GLOBAL	Separates aqueous magnesium chloride from silica and tailings residue.	Outlet Stream: PYR-SIO2 Split Fraction: PYROXENE = 1 SIO2 = 1
SEP-2	Sep	GLOBAL	Removes regenerated acid from product stream.	Outlet Stream: ACID Split Fraction: HCL= 1 WATER = 1
SEP-3	Sep	GLOBAL	Removes magnesium carbonate product from process.	Outlet Stream: MGCO3 Split Fraction: MGCO3 = 1
PH-ADJ	RStoich	ELECNRTL	Uses sodium hydroxide to adjust pH to alkaline conditions.	Flash Type: Temperature-Pressure Temperature: 25 °C Pressure: 1 atm Reactions: $NaOH+HCl\rightarrow NaCl+H_2O$
MIN-CARB	RStoich	ELECNRTL	The stable carbonate compound is produced from magnesium chloride.	Flash Type: Temperature-Pressure Temperature: 20 °C Pressure: 1 atm Reactions: $MgCl_2+H_2O+CO_2\rightarrow MgCO_3+2HCl$
SPLIT-1	Fsplit	GLOBAL	Recycles unreacted pyroxene to	Stream: PYR-REC Split Fraction: 0.8

			dissolution reactor.	
SPLIT-2	Fsplit	GLOBAL	Recycles regenerated acid to dissolution reactor.	Stream: ACID-REC Split Fraction: 0.85
SPLIT-3	Fsplit	GLOBAL	Recycles unreacted magnesium chloride solution to carbonation reactor.	Stream: SOL-REC Split Fraction: 0.85

A.5 Direct Aqueous Carbonation Process

Table A-5: Initialisation data for Aspen model of direct aqueous process

Block ID	Aspen Model	Property Method	Purpose	Input Specifications
HEATER-1	Heater	ELECNRTL	Preheats the feed stream of mineral prior to carbonation.	Flash Type: Temperature-Pressure Temperature: 185 °C Pressure: 1 atm
HEATER-2	Heater	UNIQUAC	Preheats the feed stream of carbon dioxide prior to carbonation.	Flash Type: Temperature-Pressure Temperature:185°C Pressure: 150 atm
HEATER-3	Heater	ELECNRTL	Heats feed water stream prior to carbonation.	Flash Type: Temperature-Pressure Temperature: 185 °C Pressure: 150 atm
MIX-REAC	RStoich	ELECNRTL	The production of carbonic acid from water and carbon dioxide.	Flash Type: Temperature-Pressure Temperature: 185 °C Pressure: 150 atm Reactions:$H_2O+CO_2 \rightarrow H_2CO_3$
CRB-REAC	RStoich	ELECNRTL	The production of stable carbonate from reaction of mineral with carbonic acid	Flash Type: Temperature-Pressure Temperature: 185 °C Pressure: 150 atm Reactions: $MgSiO_3+H_2CO_3 \rightarrow MgCO_3+SiO_3+H_2O$
SEP-1	Sep	GLOBAL	Separates solid product chloride from aqueous solution.	Outlet Stream: SOLIDS Split Fraction: PYROXENE = 1 SIO2 = 1 MGCO3 = 1

SEP-2	Sep	GLOBAL	Separates stable carbonate product	Outlet Stream: SIO-PYR Split Fraction: PROX= 1 SIO2 = 1
SPLIT-1	Fsplit	GLOBAL	Recycles unreacted pyroxene to dissolution reactor.	Stream: PYR-REC Split Fraction: 0.9
SPLIT-2	Fsplit	GLOBAL	Recycles regenerated acid to dissolution reactor.	Stream: ACID-REC Split Fraction: 0.95

Material Balances for Mineral Carbonation Processes

B.1.: Ammonium Salts Process

Table B- 1: Mass balance for ammonium salts process at 30% extraction

	PYROX	NH4HSO4	PYROX-FD	BISUL-FD	PYR-REC	BIS-REC	SLURRY	SIO2-PYR	SIO2-PRD	LEACH-1	LEACH-2	NH4OH	LEACH-3	CARB-FD	NH4HCO3-	CARB-PRD	MGCO3	SULF-SOL	CO2	CO2-	CO2-IN	CAP-H2O	CAP-NH3	NH4HCO3	NH3	NH4-HCO3	EVAP-FD	EVAP-FD-	EVAP-PRD	COND-PRD	DEC-FD	DEC-FD-	DEC-PRD	AMON-REC	RECYCLE	BIS-H2O	RECYCLE-	BIS-PRD
Substream: MIXED																																						
Mole Flowkmol/hr																																						
PYROX	22.70	0.	22.70	0.	28.89	0.	36.11	36.11	7.22	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	9.00	0.	9.00	0.	34.65	12.70	0.	0.	12.70	12.70	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	43.32	43.32	43.32	0.	43.32	8.66
MGSO4	0.	0.	0.	0.	0.	1.35	16.82	0.	0.	16.82	16.82	0.	16.82	16.82	0.	1.68	0.	1.68	0.	0.	0.	0.	0.	0.	0.	0.	1.68	1.68	0.	0.	1.68	1.68	1.68	1.68	1.68	0.	1.68	0.336
SIO2	0.	0.	0.	61.91	0.	77.39	77.39	15.48	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	15.48	0.	0.	15.48	15.48	0.	28.18	28.18	0.	43.32	0.	43.32	0.	0.	0.	0.	0.	0.	0.	0.	43.32	43.32	0.	0.	43.32	43.32	0.	0.	0.	0.	0.	0.
WATER	0.	357.14	0.	357.14	0.	1 140.46	1 513.08	0.	0.	1 513.08	1 513.08	355.56	1 881.33	1 881.33	101.79	1 952.84	0.	1 952.84	0.	0.	0.	527.27	0.	489.39	387.59	101.79	1 952.84	1 952.84	1 757.56	1 757.56	195.28	195.28	195.28	195.28	195.28	1 230.29	1 425.57	285.11
NH4OH	0.	0.	0.	0.	0.	0.402	0.402	0.	0.	0.402	0.402	12.80	0.502	0.502	0.	0.502	0.	0.502	0.	0.	0.	0.	0.	0.	0.	0.	0.502	0.502	0.	0.	0.502	0.502	0.502	0.502	0.502	0.	0.502	0.1
NH4HCO3	0.	0.	0.	0.	0.	30.32	30.32	0.	0.	30.32	30.32	0.	30.32	30.32	37.86	37.90	0.	37.90	0.	0.	0.	0.	0.	37.86	0.	37.86	37.90	37.90	0.	0.	37.90	37.90	37.90	37.90	37.90	0.	37.90	7.58
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	15.14	15.14	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	15.14	0.	15.14	15.14	15.14	22.72	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	43.32	5.46	5.46	0.	0.	0.	0.	0.	0.	0.	43.32	43.32	0.	0.	0.	0.
Mole Frac																																						
PYROX	1.00	0.	1.00	0.	0.318	0.	0.021	0.318	0.318	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	0.025	0.	0.025	0.	0.029	0.007	0.	0.	0.008	0.008	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.135	0.135	0.155	0.	0.029	0.029
MGSO4	0.	0.	0.	0.	0.	0.001	0.01	0.	0.	0.011	0.011	0.	0.009	0.009	0.	0.001	0.	0.001	0.	0.	0.	0.	0.	0.	0.	0.	0.001	0.001	0.	0.	0.006	0.006	0.005	0.005	0.006	0.	0.001	0.001
SIO2	0.	0.	0.	0.682	0.	0.045	0.682	0.682	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	0.009	0.	0.	0.01	0.01	0.	0.014	0.014	0.	0.021	0.	0.021	0.	0.	0.	0.	0.	0.	0.	0.	0.021	0.021	0.	0.	0.155	0.155	0.	0.	0.	0.	0.	0.
WATER	0.	0.975	0.	0.975	0.	0.945	0.889	0.	0.	0.952	0.952	0.965	0.961	0.961	0.729	0.945	0.	0.952	0.	0.	0.	1.00	0.	0.919	0.986	0.729	0.959	0.959	1.00	1.00	0.701	0.701	0.606	0.606	0.701	1.00	0.945	0.945
NH4OH	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.035	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.002	0.002	0.002	0.002	0.002	0.	0.	0.
NH4HCO3	0.	0.	0.	0.	0.	0.025	0.018	0.	0.	0.019	0.019	0.	0.015	0.015	0.271	0.018	0.	0.018	0.	0.	0.	0.	0.	0.071	0.	0.271	0.019	0.019	0.	0.	0.136	0.136	0.118	0.118	0.136	0.	0.025	0.025
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.007	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.007	0.	0.007	1.00	1.00	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	1.00	0.01	0.014	0.	0.	0.	0.	0.	0.	0.	0.135	0.135	0.	0.	0.	0.
Mass Flow kg/hr																																						
PYROX	2 278.82	0.	2 278.82	0.	2 900.32	0.	3 625.40	3 625.40	725.08	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	1 035.99	0.	1 035.99	0.	3 989.04	1 461.85	0.	0.	1 461.85	1 461.85	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	4 986.30	4 986.30	4 986.30	0.	4 986.30	997.26
MGSO4	0.	0.	0.	0.	0.	162.00	2 024.98	0.	0.	2 024.98	2 024.98	0.	2 024.98	2 024.98	0.	202.50	0.	202.50	0.	0.	0.	0.	0.	0.	0.	0.	202.50	202.50	0.	0.	202.50	202.50	202.50	202.50	202.50	0.	202.50	40.50
SIO2	0.	0.	0.	0.	3 719.76	0.	4 649.71	4 649.71	929.94	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	2 045.18	0.	0.	2 045.18	2 045.18	0.	3 723.31	3 723.31	0.	5 724.03	0.	5 724.03	0.	0.	0.	0.	0.	0.	0.	0.	5 724.03	5 724.03	0.	0.	5 724.03	5 724.03	0.	0.	0.	0.	0.	0.
WATER	0.	6 433.98	0.	6 433.98	0.	20 545.70	27 258.48	0.	0.	27 258.48	27 258.48	6 405.43	33 892.70	33 892.70	1 833.82	35 180.99	0.	35 180.99	0.	0.	0.	9 498.87	0.	8 816.42	6 982.61	1 833.82	35 180.99	35 180.99	31 662.89	31 662.89	3 518.10	3 518.10	3 518.10	3 518.10	3 518.10	22 164.02	25 682.12	5 136.42
NH4OH	0.	0.	0.	0.	0.	14.07	14.07	0.	0.	14.07	14.07	448.59	17.59	17.59	0.	17.59	0.	17.59	0.	0.	0.	0.	0.	0.	0.	0.	17.59	17.59	0.	0.	17.59	17.59	17.59	17.59	17.59	0.	17.59	3.52
NH4HCO3	0.	0.	0.	0.	2 396.71	2 396.71	2 396.71	0.	0.	2 396.71	2 396.71	0.	2 396.71	2 396.71	2 993.11	2 995.89	0.	2 995.89	0.	0.	0.	0.	0.	2 993.11	0.	2 993.11	2 995.89	2 995.89	0.	0.	2 995.89	2 995.89	2 995.89	2 995.89	2 995.89	0.	2 995.89	599.18
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	2 094.88	2 094.88	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	666.34	0.	666.34	666.34	666.34	999.90	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	737.72	92.93	92.93	0.	0.	0.	0.	0.	0.	0.	737.72	737.72	0.	0.	0.	0.
Mass Frac																																						
PYROX	1.00	0.	1.00	0.	0.438	0.	0.083	0.438	0.438	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	0.139	0.	0.139	0.	0.147	0.034	0.	0.	0.042	0.042	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.4	0.4	0.425	0.	0.147	0.147
MGSO4	0.	0.	0.	0.	0.	0.006	0.047	0.	0.	0.058	0.058	0.	0.048	0.048	0.	0.004	0.	0.005	0.	0.	0.	0.	0.	0.	0.	0.	0.005	0.005	0.	0.	0.016	0.016	0.016	0.016	0.017	0.	0.006	0.006
SIO2	0.	0.	0.	0.	0.562	0.	0.107	0.562	0.562	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	0.047	0.	0.	0.058	0.058	0.	0.089	0.089	0.	0.122	0.	0.128	0.	0.	0.	0.	0.	0.	0.	0.	0.13	0.13	0.	0.	0.459	0.459	0.	0.	0.	0.	0.	0.
WATER	0.	0.861	0.	0.861	0.	0.758	0.627	0.	0.	0.774	0.774	0.935	0.806	0.806	0.38	0.75	0.	0.786	0.	0.	0.	1.00	0.	0.741	0.987	0.38	0.797	0.797	1.00	1.00	0.282	0.282	0.282	0.282	0.3	1.00	0.758	0.758
NH4OH	0.	0.	0.	0.	0.	0.001	0.	0.	0.	0.	0.	0.065	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.001	0.001	0.001	0.001	0.002	0.	0.001	0.001
NH4HCO3	0.	0.	0.	0.	0.	0.088	0.055	0.	0.	0.068	0.068	0.	0.057	0.057	0.62	0.064	0.	0.067	0.	0.	0.	0.	0.	0.251	0.	0.62	0.068	0.068	0.	0.	0.24	0.24	0.24	0.24	0.256	0.	0.088	0.088
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.045	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.014	0.	0.015	1.00	1.00	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	1.00	0.008	0.013	0.	0.	0.	0.	0.	0.	0.	0.059	0.059	0.	0.	0.	0.
Total Flow kmol/hr	22.70	366.14	22.70	366.14	90.80	1 207.18	1 702.29	113.50	22.70	1 588.79	1 588.79	368.36	1 957.15	1 957.15	139.65	2 066.52	15.14	2 051.38	15.14	15.14	22.72	527.27	43.32	532.70	393.05	139.65	2 036.24	2 036.24	1 757.56	1 757.56	278.68	278.68	322.00	322.00	278.68	1 230.29	1 508.97	301.79
Total Flow kg/hr	2 278.82	7 469.97	2 278.82	7 469.97	6 620.09	27 107.52	43 476.38	8 275.11	1 655.02	35 201.27	35 201.27	6 854.02	42 055.29	42 055.29	4 826.93	46 882.22	2 094.88	44 787.33	666.34	666.34	999.90	9 498.87	737.72	11 902.47	7 075.54	4 826.93	44 120.99	44 120.99	31 662.89	31 662.89	12 458.10	12 458.10	12 458.10	12 458.10	11 720.38	22 164.02	33 884.40	6 776.88
Total Flow																																						
Temperature C	25	25	90	90	90		90	90	90	90	25	25	25	80	80	80	80	80	80	10	10	10	90	10	10	10	80	120	120	10	120	300	300	90	90	10		
Pressure atm	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Table B- 2: Mass balance for ammonium salts process at 50% extraction

	PYROX	NH4HSO4	PYROX-FD	BISULF-FD	PYR-REC	BIS-REC	SLURRY	SIO2-PYR	SIO2-PRD	LEACH-1	LEACH-2	NH4OH	LEACH-3	CARB-FD	NH4HCO3-	CARB-PRD	MGCO3	SULF-SOL	CO2	CO2-	CO2-IN	CAP-H2O	CAP-NH3	NH4HCO3	NH3	NH4-HCO3	EVAP-FD	EVAP-FD-	EVAP-PRD	COND-PRD	DEC-FD	DEC-FD-	DEC-PRD	AMON-REC	RECYCLE	BIS-H2O	RECYCLE-	BIS-PRD
Substream: MIXED																																						
Mole Flow kmol/hr																																						
PYROX	22.70	0.	22.70	0.	15.13	0.	18.92	18.92	3.78	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	9.00	0.	9.00	0.	34.36	5.52	0.	0.	5.52	5.52	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	42.94	42.94	42.94	0.	42.94	8.59
MGSO4	0.	0.	0.	0.	0.	1.64	20.56	0.	0.	20.56	20.56	0.	20.56	20.56	0.	2.06	0.	2.06	0.	0.	0.	0.	0.	0.	0.	0.	2.06	2.06	0.	0.	2.06	2.06	2.06	2.06	2.06	0.	2.06	0.411
SIO2	0.	0.	0.	0.	75.67	0.	94.58	94.58	18.92	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	18.92	0.	0.	18.92	18.92	0.	24.44	24.44	0.	42.94	0.	42.94	0.	0.	0.	0.	0.	0.	0.	0.	42.94	42.94	0.	0.	42.94	42.94	0.	0.	0.	0.	0.	0.
WATER	0.	357.14	0.	357.14	0.	797.76	1 173.82	0.	0.	1 173.82	1 173.82	155.56	1 334.89	1 334.89	68.14	1 366.02	0.	1366.02	0.	0.	0.	368.83	0.	327.59	259.45	68.14	1 366.02	1 366.02	1 229.42	1 229.42	136.60	136.60	136.60	136.60	136.60	860.59	997.20	199.44
NH4OH	0.	0.	0.	0.	0.	0.313	0.313	0.	0.	0.313	0.313	5.60	0.391	0.391	0.	0.391	0.	0.391	0.	0.	0.	0.	0.	0.	0.	0.	0.391	0.391	0.	0.	0.391	0.391	0.391	0.391	0.391	0.	0.391	0.078
NH4HCO3	0.	0.	0.	0.	0.	16.86	16.86	0.	0.	16.86	16.86	0.	16.86	16.86	41.23	21.07	0.	21.07	0.	0.	0.	0.	0.	41.23	0.	41.23	21.07	21.07	0.	0.	21.07	21.07	21.07	21.07	21.07	0.	21.07	4.21
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	18.51	18.51	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	18.51	0.	18.51	18.51	18.51	22.72	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	42.94	1.72	1.72	0.	0.	0.	0.	0.	0.	0.	42.94	42.94	0.	0.	0.	0.
Mole Frac																																						
PYROX	1.00	0.	1.00	0.	0.167	0.	0.014	0.167	0.167	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	0.025	0.	0.025	0.	0.04	0.004	0.	0.	0.004	0.004	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.175	0.175	0.211	0.	0.04	0.04
MGSO4	0.	0.	0.	0.	0.	0.002	0.015	0.	0.	0.017	0.017	0.	0.015	0.015	0.	0.001	0.	0.001	0.	0.	0.	0.	0.	0.	0.	0.	0.001	0.001	0.	0.	0.01	0.01	0.008	0.008	0.01	0.	0.002	0.002
SIO2	0.	0.	0.	0.	0.833	0.	0.07	0.833	0.833	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	0.014	0.	0.	0.015	0.015	0.	0.017	0.017	0.	0.029	0.	0.03	0.	0.	0.	0.	0.	0.	0.	0.	0.03	0.03	0.	0.	0.211	0.211	0.	0.	0.	0.	0.	0.
WATER	0.	0.975	0.	0.975	0.	0.938	0.87	0.	0.	0.95	0.95	0.965	0.955	0.955	0.623	0.93	0.	0.941	0.	0.	0.	1.00	0.	0.884	0.993	0.623	0.954	0.954	1.00	1.00	0.673	0.673	0.555	0.555	0.673	1.00	0.938	0.938
NH4OH	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.035	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.002	0.002	0.002	0.002	0.002	0.	0.	0.
NH4HCO3	0.	0.	0.	0.	0.	0.02	0.012	0.	0.	0.014	0.014	0.	0.012	0.012	0.377	0.014	0.	0.015	0.	0.	0.	0.	0.	0.111	0.	0.377	0.015	0.015	0.	0.	0.104	0.104	0.086	0.086	0.104	0.	0.02	0.02
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.013	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.013	0.	0.013	1.00	1.00	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	1.00	0.005	0.007	0.	0.	0.	0.	0.	0.	0.	0.175	0.175	0.	0.	0.	0.
Mass Flow kg/hr																																						
PYROX	2 278.82	0.	2 278.82	0.	1 519.22	0.	1 899.02	1 899.02	379.80	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	1 035.99	0.	1 035.99	0.	3 954.61	635.61	0.	0.	635.61	635.61	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	4 943.27	4 943.27	4 943.27	0.	4 943.27	988.65
MGSO4	0.	0.	0.	0.	0.	198.00	2 474.97	0.	0.	2 474.97	2 474.97	0.	2 474.97	2 474.97	0.	247.50	0.	247.50	0.	0.	0.	0.	0.	0.	0.	0.	247.50	247.50	0.	0.	247.50	247.50	247.50	247.50	247.50	0.	247.50	49.50
SIO2	0.	0.	0.	0.	4 546.38	0.	5 682.97	5 682.97	1 136.60	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	2 499.66	0.	0.	2 499.66	2 499.66	0.	3 229.31	3 229.31	0.	5 674.63	0.	5674.63	0.	0.	0.	0.	0.	0.	0.	0.	0.	5 674.63	5 674.63	0.	0.	5 674.63	5 674.63	0.	0.	0.	0.	0.
WATER	0.	6 433.98	0.	6 433.98	0.	14 371.80	21 146.60	0.	0.	21 146.60	21 146.60	2 802.38	24 048.45	24 048.45	1 227.56	24 609.24	0.	24609.24	0.	0.	0.	6 644.50	0.	5 901.71	4 674.15	1 227.56	24 609.24	24 609.24	22 148.32	22 148.32	2 460.93	2 460.93	2 460.93	2 460.93	2 460.93	15 503.82	17 964.75	3592.95
NH4OH	0.	0.	0.	0.	0.	10.97	10.97	0.	0.	10.97	10.97	196.26	13.71	13.71	0.	13.71	0.	13.71	0.	0.	0.	0.	0.	0.	0.	0.	13.71	13.71	0.	0.	13.71	13.71	13.71	13.71	13.71	0.	13.71	2.74
NH4HCO3	0.	0.	0.	0.	0.	1 332.74	1 332.74	0.	0.	1 332.74	1 332.74	0.	1 332.74	1 332.74	3 259.10	1 665.93	0.	1665.93	0.	0.	0.	0.	0.	3 259.10	0.	3259.10	1 665.93	1 665.93	0.	0.	1 665.93	1 665.93	1 665.93	1 665.93	1 665.93	0.	1 665.93	333.19
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	2 560.41	2 560.41	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	814.42	0.	814.42	814.42	814.42	999.90	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	731.36	29.27	29.27	0.	0.	0.	0.	0.	0.	0.	731.36	731.36	0.	0.	0.	0.
Mass Frac																																						
PYROX	1.00	0.	1.00	0.	0.25	0.	0.053	0.25	0.25	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	0.139	0.	0.139	0.	0.199	0.018	0.	0.	0.023	0.023	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.491	0.491	0.53	0.	0.199	0.199
MGSO4	0.	0.	0.	0.	0.	0.01	0.069	0.	0.	0.088	0.088	0.	0.08	0.08	0.	0.007	0.	0.007	0.	0.	0.	0.	0.	0.	0.	0.	0.008	0.008	0.	0.	0.025	0.025	0.025	0.025	0.027	0.	0.01	0.01
SIO2	0.	0.	0.	0.	0.75	0.	0.159	0.75	0.75	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	0.07	0.	0.	0.089	0.089	0.	0.104	0.104	0.	0.159	0.	0.172	0.	0.	0.	0.	0.	0.	0.	0.	0.176	0.176	0.	0.	0.564	0.564	0.	0.	0.	0.	0.	0.
WATER	0.	0.861	0.	0.861	0.	0.723	0.593	0.	0.	0.753	0.753	0.935	0.773	0.773	0.274	0.692	0.	0.745	0.	0.	0.	1.00	0.	0.642	0.994	0.274	0.764	0.764	1.00	1.00	0.245	0.245	0.245	0.245	0.264	1.00	0.723	0.723
NH4OH	0.	0.	0.	0.	0.	0.001	0.	0.	0.	0.	0.	0.065	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.001	0.001	0.001	0.001	0.001	0.	0.001	0.001
NH4HCO3	0.	0.	0.	0.	0.	0.067	0.037	0.	0.	0.047	0.047	0.	0.043	0.043	0.726	0.047	0.	0.05	0.	0.	0.	0.	0.	0.355	0.	0.726	0.052	0.052	0.	0.	0.166	0.166	0.166	0.166	0.179	0.	0.067	0.067
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.072	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.023	0.	0.025	1.00	1.00	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	1.00	0.003	0.006	0.	0.	0.	0.	0.	0.	0.	0.073	0.073	0.	0.	0.	0.
Total Flow kmol/hr	22.70	366.14	22.70	366.14	90.80	850.93	1 349.49	113.50	22.70	1 235.99	1 235.99	161.16	1 397.14	1 397.14	109.37	1 469.50	18.51	1450.99	18.51	18.51	22.72	368.83	42.94	370.54	261.17	109.37	1 432.49	1 432.49	1 229.42	1 229.42	203.07	203.07	246.01	246.01	203.07	860.59	1 063.66	212.73
Total Flow kg/hr	2 278.82	7 469.97	2 278.82	7 469.97	6 065.59	19 868.12	35 682.54	7 581.99	1 516.40	28 100.55	28 100.55	2 998.63	31 099.18	31 099.18	4 486.66	35 585.84	2 560.41	33025.43	814.42	814.42	999.90	6 644.50	731.36	9 190.08	4 703.42	4 486.66	32 211.01	32 211.01	22 148.32	22 148.32	10 062.69	10 062.69	10 062.69	10 062.69	9 331.33	15 503.82	24 835.15	4 967.03
Total Flow																																						
Temperature C	25	25	90	90	90		90	90	90	90	25	25	25	80	80	80	80	80	80	10	10	10	90	10	10	10	80	120	120	10	120	300	300	90	90	10			
Pressure atm	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Table B- 3: Mass balance for ammonium salts process at 90% extraction

	PYROX	NH4HSO4	PYROX-FD	BISUL-FD	PYR-REC	BIS-REC	SLURRY	SIO2-PYR	SIO2-PRD	LEACH-1	LEACH-2	NH4OH	LEACH-3	CARB-FD	NH4HCO3-	CARB-PRD	MGCO3	SULF-SOL	CO2	CO2-	CO2-IN	CAP-H2O	CAP-NH3	NH4HCO3	NH3	NH4-HCO3	EVAP-FD	EVAP-FD-	EVAP-PRD	COND-PRD	DEC-FD	DEC-FD-	DEC-PRD	AMON-REC	RECYCLE	BIS-H2O	RECYCLE-	BIS-PRD
Substream: MIXED																																						
Mole Flow kmol/hr																																						
PYROX	22.70	0.	22.70	0.	1.97	0.	2.47	2.47	0.493	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	10.00	0.	10.00	0.	38.07	3.66	0.	0.	3.66	3.66	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	47.59	47.59	47.59	0.	47.59	9.52
MGSO4	0.	0.	0.	0.	0.	1.93	24.14	0.	0.	24.14	24.14	0.	24.14	24.14	0.	2.41	0.	2.41	0.	0.	0.	0.	0.	0.	0.	0.	2.41	2.41	0.	0.	2.41	2.41	2.41	2.41	2.41	0.	2.41	0.483
SIO2	0.	0.	0.	0.	88.83	0.	111.03	111.03	22.21	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	22.21	0.	0.	22.21	22.21	0.	25.86	25.86	0.	47.59	0.	47.59	0.	0.	0.	0.	0.	0.	0.	0.	47.59	47.59	0.	0.	47.59	47.59	0.	0.	0.	0.	0.	0.
WATER	0.	396.83	0.	396.83	0.	767.29	1 186.33	0.	0.	1 186.33	1 186.33	102.78	1 292.76	1 292.76	64.54	1 313.86	0.	1 313.86	0.	0.	0.	354.74	0.	310.30	245.76	64.54	1 313.86	1 313.86	1 182.47	1 182.47	131.39	131.39	131.39	131.39	131.39	827.73	959.12	191.82
NH4OH	0.	0.	0.	0.	0.	0.176	0.176	0.	0.	0.176	0.176	3.70	0.22	0.22	0.	0.22	0.	0.22	0.	0.	0.	0.	0.	0.	0.	0.	0.22	0.22	0.	0.	0.22	0.22	0.22	0.22	0.22	0.	0.22	0.044
NH4HCO3	0.	0.	0.	0.	0.	3.98	3.98	0.	0.	3.98	3.98	0.	3.98	3.98	44.44	4.98	0.	4.98	0.	0.	0.	0.	0.	44.44	0.	44.44	4.98	4.98	0.	0.	4.98	4.98	4.98	4.98	4.98	0.	4.98	0.996
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	21.72	21.72	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	21.72	0.	21.72	21.72	21.72	22.72	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	47.59	3.14	3.14	0.	0.	0.	0.	0.	0.	0.	47.59	47.59	0.	0.	0.	0.
Mole Frac																																						
PYROX	1.00	0.	1.00	0.	0.022	0.	0.002	0.022	0.022	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	0.025	0.	0.025	0.	0.047	0.003	0.	0.	0.003	0.003	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.203	0.203	0.255	0.	0.047	0.047
MGSO4	0.	0.	0.	0.	0.	0.002	0.018	0.	0.	0.019	0.019	0.	0.018	0.018	0.	0.002	0.	0.002	0.	0.	0.	0.	0.	0.	0.	0.	0.002	0.002	0.	0.	0.013	0.013	0.01	0.01	0.013	0.	0.002	0.002
SIO2	0.	0.	0.	0.	0.978	0.	0.082	0.978	0.978	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	0.016	0.	0.	0.018	0.018	0.	0.019	0.019	0.	0.034	0.	0.034	0.	0.	0.	0.	0.	0.	0.	0.	0.035	0.035	0.	0.	0.255	0.255	0.	0.	0.	0.	0.	0.
WATER	0.	0.975	0.	0.975	0.	0.946	0.876	0.	0.	0.956	0.956	0.965	0.96	0.96	0.592	0.93	0.	0.945	0.	0.	0.	1.00	0.	0.867	0.987	0.592	0.96	0.96	1.00	1.00	0.704	0.704	0.561	0.561	0.704	1.00	0.946	0.946
NH4OH	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.035	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.001	0.001	0.001	0.001	0.001	0.	0.	0.
NH4HCO3	0.	0.	0.	0.	0.	0.005	0.003	0.	0.	0.003	0.003	0.	0.003	0.003	0.408	0.004	0.	0.004	0.	0.	0.	0.	0.	0.124	0.	0.408	0.004	0.004	0.	0.	0.027	0.027	0.021	0.021	0.027	0.	0.005	0.005
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.015	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.015	0.	0.016	1.00	1.00	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	1.00	0.009	0.013	0.	0.	0.	0.	0.	0.	0.	0.203	0.203	0.	0.	0.	0.
Mass Flow kg/hr																																						
PYROX	2 278.82	0.	2 278.82	0.	198.16	0.	247.70	247.70	49.54	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	1 151.10	0.	1 151.10	0.	4 382.12	420.84	0.	0.	420.84	420.84	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	5 477.66	5 477.66	5 477.66	0.	5 477.66	1 095.53
MGSO4	0.	0.	0.	0.	0.	232.43	2 905.40	0.	0.	2 905.40	2 905.40	0.	2 905.40	2 905.40	0.	290.54	0.	290.54	0.	0.	0.	0.	0.	0.	0.	0.	290.54	290.54	0.	0.	290.54	290.54	290.54	290.54	290.54	0.	290.54	58.11
SIO2	0.	0.	0.	0.	5 337.05	0.	6 671.32	6 671.32	1 334.26	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	2 934.38	0.	0.	2 934.38	2 934.38	0.	3 417.48	3 417.48	0.	6 288.08	0.	6 288.08	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	6 288.08	6 288.08	0.	0.	0.	0.	0.
WATER	0.	7 148.92	0.	7 148.92	0.	13 822.99	21 372.04	0.	0.	21 372.04	21 372.04	1 851.57	23 289.47	23 289.47	1 162.75	23 669.51	0.	23 669.51	0.	0.	0.	6 390.77	0.	5 590.15	4 427.40	1 162.75	23 669.51	23 669.51	21 302.56	21 302.56	2 366.95	2 366.95	2 366.95	2 366.95	2 366.95	14 911.79	17 278.74	3 455.75
NH4OH	0.	0.	0.	0.	0.	6.17	6.17	0.	0.	6.17	6.17	129.67	7.72	7.72	0.	7.72	0.	7.72	0.	0.	0.	0.	0.	0.	0.	0.	7.72	7.72	0.	0.	7.72	7.72	7.72	7.72	7.72	0.	7.72	1.54
NH4HCO3	0.	0.	0.	0.	0.	315.03	315.03	0.	0.	315.03	315.03	0.	315.03	315.03	3 513.53	393.79	0.	393.79	0.	0.	0.	0.	0.	3 513.53	0.	3513.53	393.79	393.79	0.	0.	393.79	393.79	393.79	393.79	393.79	0.	393.79	78.76
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	3005.70	3 005.70	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	956.06	0.	956.06	956.06	956.06	999.90	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	810.42	53.52	53.52	0.	0.	0.	0.	0.	0.	0.	810.42	810.42	0.	0.	0.	0.
Mass Frac																																						
PYROX	1.00	0.	1.00	0.	0.036	0.	0.007	0.036	0.036	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4HSO4	0.	0.139	0.	0.139	0.	0.234	0.012	0.	0.	0.015	0.015	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.586	0.586	0.642	0.	0.234	0.234
MGSO4	0.	0.	0.	0.	0.	0.012	0.083	0.	0.	0.104	0.104	0.	0.097	0.097	0.	0.008	0.	0.009	0.	0.	0.	0.	0.	0.	0.	0.	0.009	0.009	0.	0.	0.031	0.031	0.031	0.031	0.034	0.	0.012	0.012
SIO2	0.	0.	0.	0.	0.964	0.	0.191	0.964	0.964	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH4SO4	0.	0.	0.	0.	0.	0.	0.084	0.	0.	0.105	0.105	0.	0.114	0.114	0.	0.182	0.	0.199	0.	0.	0.	0.	0.	0.	0.	0.	0.205	0.205	0.	0.	0.673	0.673	0.	0.	0.	0.	0.	0.
WATER	0.	0.861	0.	0.861	0.	0.737	0.613	0.	0.	0.765	0.765	0.935	0.778	0.778	0.249	0.684	0.	0.749	0.	0.	0.	1.00	0.	0.61	0.988	0.249	0.772	0.772	1.00	1.00	0.253	0.253	0.253	0.253	0.277	1.00	0.737	0.737
NH4OH	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.065	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.001	0.001	0.001	0.001	0.001	0.	0.	0.
NH4HCO3	0.	0.	0.	0.	0.	0.017	0.009	0.	0.	0.011	0.011	0.	0.011	0.011	0.751	0.011	0.	0.012	0.	0.	0.	0.	0.	0.384	0.	0.751	0.013	0.013	0.	0.	0.042	0.042	0.042	0.042	0.046	0.	0.017	0.017
MGCO3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.087	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CO2	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.028	0.	0.03	1.00	1.00	1.00	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NH3	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	1.00	0.006	0.012	0.	0.	0.	0.	0.	0.	0.	0.087	0.087	0.	0.	0.	0.
Total Flow kmol/hr	22.70	406.83	22.70	406.83	90.80	811.45	1 353.99	113.50	22.70	1 240.49	1 240.49	106.48	1 346.97	1 346.97	108.99	1 412.51	21.72	1 390.78	21.72	21.72	22.72	354.74	47.59	357.89	248.90	108.99	1 369.06	1 369.06	1 182.47	1 182.47	186.59	186.59	234.17	234.17	186.59	827.73	1 014.32	202.86
Total Flow kg/hr	2 278.82	8 300.02	2 278.82	8 300.02	5 535.21	18 758.75	34 872.88	6 919.02	1 383.80	27 953.87	27 953.87	1 981.24	29 935.11	29 935.11	4 676.28	34 611.39	3 005.70	31 605.69	956.06	956.06	999.90	6 390.77	810.42	9 157.20	4 480.92	4 676.28	30 649.63	30 649.63	21 302.56	21 302.56	9 347.07	9 347.07	9 347.07	9347.07	8 536.65	14 911.79	23 448.44	4 689.69
Total Flow																																						
Temperature C	25	25	90	90	90		90	90	90	25	25	25	80	80	80	80	80	80	80	10	10	10	90	10	10	10	80	120	120	10	120	300	300	90	90	10			
Pressure atm	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

B.2.: Lackner's HCl Mutli-stage Process

Table B- 4: Mass balance for Lackner's multi-stage process at 30% extraction

	PYROX	HCL	PYROX-FD	HCL-FD	PYR-REC	HCL-REC	SLURRY-1	PYR-SIO2	SIO2-PYR	MGCL2-W	MGOHCL-H	HCL-H2	HCL-STR	MGOHCL	SLURRY-2	H2O-2	MGOH	CO2	MGCO3-H2	H2O	MGCO3	HCL-PRD
Substream: MIXED																						
Mole Flow kmol/hr																						
PYROX	56.1	0	56.1	0	95.52	0	106.14	106.14	10.61	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	50.1	0	50.1	0	41.52	0.649	0	0	0.649	46.14	46.14	46.14	0	0	0	0	0	0	0	0	4.61
WATER	0	1391.67	0	1391.67	0	3578.57	4742.81	0	0	4742.81	4970.24	3976.19	3976.19	994.05	994.05	994.05	0	0	22.72	22.72	0	397.62
MGCL2-W	0	0	0	0	0	0	45.49	0	0	45.49	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	409.37	0	454.86	454.86	45.49	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	45.49	0	0	45.49	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.74	0	22.74	0	0.023	0	0.023	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.74	22.74	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.72	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.72	0	22.72	0
Mole Frac																						
PYROX	1	0	1	0	0.189	0	0.020	0.189	0.189	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.035	0	0.035	0	0.011	1.21E-04	0	0	1.36E-04	0.009	0.011	0.011	0	0	0	0	0	0	0	0	0.011
WATER	0	0.965	0	0.965	0	0.989	0.887	0	0	0.990	0.982	0.989	0.989	0.956	0.956	0.978	0	0	0.500	1	0	0.989
MGCL2-W	0	0	0	0	0	0	0.009	0	0	0.009	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0.811	0	0.085	0.811	0.811	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	0.009	0	0	0.044	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.022	0	1	0	0.001	0	0.001	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.022	0.022	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.500	0	0.999	0
Mass Flow kg/hr																						
PYROX	5631.81	0	5631.81	0	9589.29	0	10654.77	10654.77	1065.48	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	1826.68	0	1826.68	0	1513.92	23.67	0	0	23.67	1682.13	1682.13	1682.13	0	0	0	0	0	0	0	0	168.21
WATER	0	25071.27	0	25071.27	0	64468.98	85442.99	0	0	85442.99	89540.25	71632.20	71632.20	17908.05	17908.05	17908.05	0	0	409.31	409.31	0	7163.22
MGCL2-W	0	0	0	0	0	0	9247.50	0	0	9247.50	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	24596.88	0	27329.86	27329.86	2732.99	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	3491.77	0	0	3491.77	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1326.38	0	1326.38	0	1.36	0	1.36	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2165.39	2165.39	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	999.90	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1915.62	0	1915.62	0
Mass Frac																						
PYROX	1	0	1	0	0.281	0	0.080	0.281	0.281	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.068	0	0.068	0	0.023	1.78E-04	0	0	2.50E-04	0.018	0.023	0.023	0	0	0	0	0	0	0	0	0.023
WATER	0	0.932	0	0.932	0	0.977	0.644	0	0	0.902	0.945	0.977	0.977	0.837	0.837	0.892	0	0	0.176	1	0	0.977
MGCL2-W	0	0	0	0	0	0	0.070	0	0	0.098	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0.719	0	0.206	0.719	0.719	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	0.037	0	0	0.163	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.062	0	1	0	0.001	0	0.001	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.101	0.108	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.823	0	0.999	0
Total Flow kmol/hr	56.10	1441.77	56.10	1441.77	504.89	3620.09	5349.94	560.99	56.10	4788.94	5061.86	4022.33	4022.33	1039.53	1039.53	1016.79	22.74	22.72	45.46	22.72	22.74	402.23
Total Flow kg/hr	5631.81	26897.95	5631.81	26897.95	34186.17	65982.90	132699.00	37984.63	3798.46	94714.16	94714.16	73314.34	73314.34	21399.82	21399.82	20073.44	1326.38	999.90	2326.28	409.31	1916.97	7331.43
Total Flow																						
Temperature C	25	25	70	70	70	70	70	70	70	70	150	150	70	150	70	70	70	25	407	407	407	70
Pressure atm	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	57.48	1	1	1	1

Table B- 5: Mass balance for Lackner's multi-stage process at 50% extraction

	PYROX	HCL	PYROX-FD	HCL-FD	PYR-REC	HCL-REC	SLURRY-1	PYR-SIO2	SIO2-PYR	MGCL2-W	MGOHCL-H	HCL-H2	HCL-STR	MGOHCL	SLURRY-2	H2O-2	MGOH	CO2	MGCO3-H2	H2O	MGCO3	HCL-PRD
Substream: MIXED																						
Mole Flow kmol/hr																						
PYROX	56.1	0	56.1	0	45.9	0	51	51	5.1	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	56.2	0	56.2	0	46.80	1	0	0	1	52.00	52.00	52.00	0	0	0	0	0	0	0	0	5.20
WATER	0	1561.11	0	1561.11	0	4014.29	5320.40	0	0	5320.40	5575.40	4460.32	4460.32	1115.08	1115.08	1115.08	0	0	22.72	22.72	0	446.03
MGCL2-W	0	0	0	0	0	0	51	0	0	51	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	458.76	0	509.74	509.74	50.97	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	51	0	0	51	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	25.5	0	25.5	0	2.78	0	2.78	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	25.5	25.5	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.72	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.72	0	22.72	0
Mole Frac																						
PYROX	1	0	1	0	0.091	0	0.009	0.091	0.091	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.035	0	0.035	0	0.012	0.000	0	0	1.86E-04	0.009	0.012	0.012	0	0	0	0	0	0	0	0	0.012
WATER	0	0.965	0	0.965	0	0.988	0.897	0	0	0.990	0.982	0.988	0.988	0.956	0.956	0.978	0	0	0.471	1	0	0.988
MGCL2-W	0	0	0	0	0	0	0.009	0	0	0.009	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0.909	0	0.086	0.909	0.909	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	0.009	0	0	0.044	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.022	0	1	0	0.058	0	0.109	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.022	0.022	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.471	0	0.891	0
Mass Flow kg/hr																						
PYROX	5631.81	0	5631.81	0	4607.84	0	5119.82	5119.82	511.98	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	2049.09	0	2049.09	0	1706.36	36.46	0	0	36.46	1895.95	1895.95	1895.95	0	0	0	0	0	0	0	0	189.60
WATER	0	28123.85	0	28123.85	0	72318.48	95848.43	0	0	95848.43	100442.00	80353.86	80353.86	20088.47	20088.47	20088.47	0	0	409.31	409.31	0	8035.39
MGCL2-W	0	0	0	0	0	0	10368.41	0	0	10368.41	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	27564.53	0	30627.26	30627.26	3062.73	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	3915.02	0	0	3915.02	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1487.15	0	1487.15	0	162.13	0	162.13	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2427.87	2427.87	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	999.90	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1915.62	0	1915.62	0
Mass Frac																						
PYROX	1	0	1	0	0.143	0	0.036	0.143	0.143	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.068	0	0.068	0	0.023	0.000	0	0	0.000	0.018	0.023	0.023	0	0	0	0	0	0	0	0	0.023
WATER	0	0.932	0	0.932	0	0.977	0.675	0	0	0.902	0.945	0.977	0.977	0.837	0.837	0.892	0	0	0.165	1	0	0.977
MGCL2-W	0	0	0	0	0	0	0.073	0	0	0.098	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0.857	0	0.216	0.857	0.857	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	0.037	0	0	0.163	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.062	0	1	0	0.065	0	0.078	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.101	0.108	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.770	0	0.922	0
Total Flow kmol/hr	56.10	1617.31	56.10	1617.31	504.66	4061.09	5933.13	560.74	56.07	5372.40	5678.40	4512.32	4512.32	1166.08	1166.08	1140.58	25.50	22.72	48.22	22.72	25.50	451.23
Total Flow kg/hr	5631.81	30172.94	5631.81	30172.94	32172.37	74024.83	142000.00	35747.08	3574.71	106253.00	106253.00	82249.81	82249.81	24003.48	24003.48	22516.33	1487.15	999.90	2487.06	409.31	2077.75	8224.98
Total Flow																						
Temperature C	25	25	70	70	70	70	70	70	70	70	150	150	70	150	70	70	70	25	407	407	407	70
Pressure atm	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	57.48	1	1	1	1

Table B- 6: Mass balance for Lackner's multi-stage process at 90% extraction

	PYROX	HCL	PYROX-FD	HCL-FD	PYR-REC	HCL-REC	SLURRY-1	PYR-SIO2	SIO2-PYR	MGCL2-W	MGOHCL-H	HCL-H2	HCL-STR	MGOHCL	SLURRY-2	H2O-2	MGOH	CO2	MGCO3-H2	H2O	MGCO3	HCL-PRD
Substream: MIXED																						
Mole Flow kmol/hr																						
PYROX	56.1	0	56.1	0	5.55	0	6.16	6.16	0.616	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	61.1	0	61.1	0	50.55	0.681	0	0	0.681	56.16	56.16	56.16	0	0	0	0	0	0	0	0	5.62
WATER	0	1697.22	0	1697.22	0	4364.29	5784.09	0	0	5784.09	6061.51	4849.21	4849.21	1212.30	1212.30	1212.30	0	0	22.72	22.72	0	484.92
MGCL2-W	0	0	0	0	0	0	55.48	0	0	55.48	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	499.35	0	554.83	554.83	55.48	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	55.48	0	0	55.48	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	27.74	0	27.74	0	5.02	0	5.02	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	27.74	27.74	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.72	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.72	0	22.72	0
Mole Frac																						
PYROX	1	0	1	0	0.011	0	0.001	0.011	0.011	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.035	0	0.035	0	0.011	0.0001	0	0	1.17E-04	0.009	0.011	0.011	0	0	0	0	0	0	0	0	0.011
WATER	0	0.965	0	0.965	0	0.989	0.904	0	0	0.990	0.982	0.989	0.989	0.956	0.956	0.978	0	0	0.450	1	0	0.989
MGCL2-W	0	0	0	0	0	0	0.009	0	0	0.010	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0.989	0	0.087	0.989	0.989	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	0.009	0	0	0.044	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.022	0	1	0	0.100	0	0.181	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.022	0.022	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.450	0	0.819	0
Mass Flow kg/hr																						
PYROX	5631.81	0	5631.81	0	556.99	0	618.88	618.88	61.89	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	2227.75	0	2227.75	0	1843.01	24.83	0	0	24.83	2047.79	2047.79	2047.79	0	0	0	0	0	0	0	0	204.78
WATER	0	30575.93	0	30575.93	0	78623.82	104202.00	0	0	104202.00	109200.00	87359.80	87359.80	21839.95	21839.95	21839.95	0	0	409.31	409.31	0	8735.98
MGCL2-W	0	0	0	0	0	0	11279.91	0	0	11279.91	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	30003.14	0	33336.82	33336.82	3333.68	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	4259.19	0	0	4259.19	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1617.89	0	1617.89	0	292.87	0	292.87	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2641.30	2641.30	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	999.90	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1915.62	0	1915.62	0
Mass Frac																						
PYROX	1	0	1	0	0.018	0	0.004	0.018	0.018	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.068	0	0.068	0	0.023	0.000	0.00E+00	0	2.15E-04	0.018	0.023	0.023	0	0	0	0	0	0	0	0	0.023
WATER	0	0.932	0	0.932	0	0.977	0.697	0	0	0.902	0.945	0.977	0.977	0.837	0.837	0.892	0	0	0.156	1	0	0.977
MGCL2-W	0	0	0	0	0	0	0.075	0	0	0.098	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0.982	0	0.223	0.982	0.982	0	0	0	0	0	0	0	0	0	0	0	0	0
MGOHCL	0	0	0	0	0	0	0	0	0	0	0.037	0	0	0.163	0	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.062	0	1	0.00E+00	0.112	0.00E+00	0.133	0
MGCL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.101	0.108	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.732	0	0.867	0
Total Flow kmol/hr	56.10	1758.32	56.10	1758.32	504.90	4414.83	6401.25	561.00	56.10	5840.25	6173.16	4905.37	4905.37	1267.79	1267.79	1240.04	27.74	22.72	50.46	22.72	27.74	490.54
Total Flow kg/hr	5631.81	32803.67	5631.81	32803.67	30560.13	80466.83	149462.00	33955.70	3395.57	115507.00	115507.00	89407.59	89407.59	26099.14	26099.14	24481.25	1617.89	999.90	2617.79	409.31	2208.49	8940.76
Total Flow																						
Temperature C	25	25	70	70	70	70	70	70	70	70	150	150	70	150	70	70	70	25	407	407	407	70
Pressure atm	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	57.48	1	1	1	1

B.3.: Åbo Akademi University (AAU) Process

Table B- 7: Mass balance for Åbo Akademi University process at 66% extraction

	A-SULF	PYROX	PYROX-FD	AS-REC	PYR-REC	ASR-PRD	NH3-H2O	SOLIDS	SOLIDS-	H2O	SLURRY-1	SIO2-PYR	SIO2	MGSO-4	NH3-H2O-	SLURRY-2	SULF-REC	MGOH	MGOH-	CO2	CO2-FD	CARB-REC	MGCO3-H2	CARB-STR	MGCO3	MGCO3-PR	CARB-PRG	CARB-H2O	H2O-OUT	AS-SOL	STEAM	AS-SOLID	AS-PRD
Substream: MIXED																																	
Mole Flow kmol/hr																																	
PYROX	0	25.5	25.5	0	11.24	12.49	0	12.49	12.49	0	12.49	12.49	1.25	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SULFATE	3	0	0	27.00	0	5.75	0	5.75	5.75	0	5.75	0	0	5.75	0	30.00	30.00	0	0	0	0	0	0	0	0	0	0	0	0	30.00	0	30.00	3.00
MGSO4	0	0	0	0	0	24.25	0	24.25	24.25	0	24.25	0	0	24.25	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	218.08	242.31	0	242.31	242.31	0	242.31	242.31	24.23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0	0	48.50	48.50	0	0	0	0	0	0	0	48.50	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0	0	0	0	24.25	24.25	0	0	47.08	47.08	0	0	47.08	24.25	22.83	22.83	0	0	0	0	0	22.42	22.42	0	0	2.24	20.17	20.17	22.83	22.83	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	24.25	0	24.25	24.25	0	0	16.51	18.34	18.34	0	0	1.83	16.51	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.72	22.72	2.75	3.06	3.06	0	0	0.31	2.75	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.42	0	22.42	22.42	0	0	0	0	0	0	0
Mole Frac																																	
PYROX	0	1	1	0	0.049	0.035	0	0.044	0.044	0	0.038	0.049	0.049	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SULFATE	1	0	0	1	0	0.016	0	0.020	0.020	0	0.017	0	0	0.075	0	0.389	0.568	0	0	0	0	0	0	0	0	0	0	0	0	0.568	0	1	1
MGSO4	0	0	0	0	0	0.068	0	0.085	0.085	0	0.073	0	0	0.315	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0.951	0.678	0	0.851	0.851	0	0.730	0.951	0.951	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0	0	0.136	0.667	0	0	0	0	0	0	0	0.667	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0	0	0	0	0.068	0.333	0	0	1	0.142	0	0	0.611	0.333	0.296	0.432	0	0	0	0	0	0.338	0.512	0	0	0.512	0.512	1	0.432	1	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.315	0	1	1	0	0	0.857	0.277	0.419	0	0	0.419	0.419	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0.143	0.046	0.070	0	0	0.070	0.070	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.338	0	1	1	0	0	0	0	0	0	0
Mass Flow kg/hr																																	
PYROX	0	2559.91	2559.91	0	1128.722	1254.14	0	1254.14	1254.14	0	1254.14	1254.14	125.41	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SULFATE	396.42	0	0	3567.46	0	759.34	0	759.34	759.34	0	759.34	0	0	759.34	0	3963.84	3963.84	0	0	0	0	0	0	0	0	0	0	0	0	3963.84	0	3963.84	396.38
MGSO4	0	0	0	0	0	2919.03	0	2919.03	2919.03	0	2919.03	0	0	2919.03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	13103.09	14558.99	0	14558.99	14558.99	0	14558.99	14558.99	1455.90	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0	0	826.01	826.01	0	0	0	0	0	0	0	826.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0	0	0	0	436.88	436.88	0	0	848.19	848.19	0	0	848.19	436.88	411.31	411.31	0	0	0	0	0	403.84	403.84	0	0	40.38	363.46	363.46	411.31	411.31	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1414.29	0	1414.29	1414.29	0	0	962.67	1069.63	1069.63	0	0	106.96	962.67	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1000	1000	121.14	134.59	134.59	0	0	13.46	121.13	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1890.04	0	1890.04	1890.04	0	0	0	0	0	0	0
Mass Frac																																	
PYROX	0	1	1	0	0.079	0.060	0	0.064	0.064	0	0.062	0.079	0.079	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SULFATE	1	0	0	1	0	0.037	0	0.039	0.039	0	0.037	0	0	0.168	0	0.685	0.906	0	0	0	0	0	0	0	0	0	0	0	0	0.906	0	1	1
MGSO4	0	0	0	0	0	0.141	0	0.150	0.150	0	0.144	0	0	0.645	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0.921	0.701	0	0.747	0.747	0	0.716	0.921	0.921	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0	0	0.040	0.654	0	0	0	0	0	0	0	0.654	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0	0	0	0	0.021	0.346	0	0	1	0.042	0	0	0.187	0.346	0.071	0.094	0	0	0	0	0	0.115	0.251	0	0	0.251	0.251	1	0.094	1	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.244	0	1	1	0	0	0.888	0.306	0.665	0	0	0.665	0.665	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0.112	0.038	0.084	0	0	0.084	0.084	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.540	0	1	1	0	0	0	0	0	0	0
Total Flow kmol/hr	3	25.5	25.5	27.00	229.32	357.55	72.75	284.80	284.80	47.08	331.88	254.80	25.48	77.08	72.75	77.08	52.83	24.25	24.25	22.72	22.72	19.26	66.23	43.82	22.42	22.42	4.38	39.43	20.17	52.83	22.83	30.00	3.00
Total Flow kg/hr	396.42	2559.91	2559.91	3567.46	14231.81	20754.37	1262.89	19491.48	19491.48	848.19	20339.67	15813.12	1581.31	4526.55	1262.89	5789.44	4375.15	1414.29	1414.29	1000	1000	1083.81	3498.10	1608.06	1890.04	1890.04	160.81	1447.26	363.46	4375.15	411.31	3963.84	396.38
Total Flow																																	
Temperature C	25	25	400	110		400	400	400	40	25					25	40	40	40	450	30	450	450	450	450	450	30	450	450	450	110	110	110	110
Pressure atm	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	19.74	19.74	19.74	19.74	19.74	19.74	19.74	19.74	19.74	19.74	1	1	1	1

Table B- 8: Mass balance for Åbo Akademi University process at 100% extraction

	A-SULF	PYROX	PYROX-FD	AS-REC	PYR-REC	ASR-PRD	NH3-H2O	SOLIDS	SOLIDS-	H2O	SLURRY-1	SIO2-PYR	SIO2	MGSO-4	NH3-H2O-	SLURRY-2	SULF-REC	MGOH	MGOH-	CO2	CO2-FD	CARB-REC	MGCO3-H2	CARB-STR	MGCO3	MGCO3-PR	CARB-PRG	CARB-H2O	H2O-OUT	AS-SOL	STEAM	AS-SOLID	AS-PRD
Substream: MIXED																																	
Mole Flow kmol/hr																																	
PYROX	0	22.72	22.72	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SULFATE	3	0	0	27.00	0	7.28	0	7.28	7.28	0	7.28	0	0	7.28	0	30.00	30.00	0	0	0	0	0	0	0	0	0	0	0	0	30.00	0	30.00	3.00
MGSO4	0	0	0	0	0	22.72	0	22.72	22.72	0	22.72	0	0	22.72	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0	22.72	0	22.72	22.72	0	22.72	22.72	22.72	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0	0	45.44	45.44	0	0	0	0	0	0	0	45.44	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0	0	0	0	22.72	22.72	0	0	47.08	47.08	0	0	47.08	22.72	24.36	24.36	0	0	0	0	0	22.17	22.17	0	0	2.22	19.95	19.95	24.36	24.36	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.72	0	22.72	22.72	0	0	4.99	5.54	5.54	0	0	0.55	4.99	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.72	22.72	5.01	5.56	5.56	0	0	0.56	5.01	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.17	0	22.17	22.17	0	0	0	0	0	0	0
Mole Frac																																	
PYROX	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SULFATE	1	0	0	1	0	0.060	0	0.138	0.138	0	0.073	0	0	0.094	0	0.389	0.552	0	0	0	0	0	0	0	0	0	0	0	0	0.552	0	1	1
MGSO4	0	0	0	0	0	0.188	0	0.431	0.431	0	0.228	0	0	0.295	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0	0.188	0	0.431	0.431	0	0.228	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0	0	0.376	0.667	0	0	0	0	0	0	0	0.667	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0	0	0	0	0.188	0.333	0	0	1	0.472	0	0	0.611	0.333	0.316	0.448	0	0	0	0	0	0.400	0.666	0	0	0.666	0.666	1	0.448	1	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.295	0	1	1	0	0	0.499	0.100	0.167	0	0	0.167	0.167	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0.501	0.100	0.167	0	0	0.167	0.167	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.400	0	1	1	0	0	0	0	0	0	0
Mass Flow kg/hr																																	
PYROX	0	2280.83	2280.83	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SULFATE	396.42	0	0	3567.44	0	961.59	0	961.59	961.59	0	961.59	0	0	961.59	0	3963.82	3963.82	0	0	0	0	0	0	0	0	0	0	0	0	3963.82	0	3963.82	396.382
MGSO4	0	0	0	0	0	2734.78	0	2734.78	2734.78	0	2734.78	0	0	2734.78	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0	1365.12	0	1365.12	1365.12	0	1365.12	1365.12	1365.12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0	0	773.87	773.87	0	0	0	0	0	0	0	773.87	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0	0	0	0	409.31	409.31	0	0	848.19	848.19	0	0	848.19	409.31	438.88	438.88	0	0	0	0	0	399.32	399.32	0	0	39.93	359.39	359.39	438.88	438.88	0	0
MGOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1325.02	0	1325.02	1325.02	0	0	290.86	323.18	323.18	0	0	32.32	290.86	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1000	1000	220.27	244.76	244.76	0	0	24.48	220.28	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1868.90	0	1868.90	1868.90	0	0	0	0	0	0	0
Mass Frac																																	
PYROX	0	1	1	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SULFATE	1	0	0	1		0.154	0	0.190	0.190	0	0.163	0	0	0.212	0	0.692	0.900	0	0	0	0	0	0	0	0	0	0	0	0	0.900	0	1	1
MGSO4	0	0	0	0		0.438	0	0.540	0.540	0	0.463	0	0	0.602	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SIO2	0	0	0	0		0.219	0	0.270	0.270	0	0.231	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0		0.124	0.654	0	0	0	0	0	0	0	0.654	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0	0	0		0.066	0.346	0	0	1	0.144	0	0	0.187	0.346	0.077	0.100	0	0	0	0	0	0.141	0.413	0	0	0.413	0.413	1	0.100	1	0	0
MGOH	0	0	0	0		0	0	0	0	0	0	0	0	0	0	0.231	0	1	1	0	0	0.569	0.114	0.334	0	0	0.334	0.334	0	0	0	0	0
CO2	0	0	0	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0.431	0.086	0.253	0	0	0.253	0.253	0	0	0	0	0
MGCO3	0	0	0	0		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.659	0	1	1	0	0	0	0	0	0	0
Total Flow kmol/hr	3	22.72	22.72	27.00	0	120.88	68.16	52.72	52.72	47.08	99.80	22.72	22.72	77.08	68.16	77.08	54.36	22.72	22.72	22.72	22.72	9.99	55.43	33.27	22.17	22.17	3.33	29.94	19.95	54.36	24.36	30.00	3.00
Total Flow kg/hr	396.42	2280.83	2280.83	3567.44	0	6244.65	1183.18	5061.48	5061.48	848.19	5909.67	1365.12	1365.12	4544.55	1183.18	5727.73	4402.70	1325.02	1325.02	1000	1000	511.13	2836.15	967.26	1868.90	1868.90	96.73	870.53	359.39	4402.70	438.88	3963.82	396.38
Total Flow cum/hr					0																												
Temperature C	25	25	400	110		400	400	400	40	25					25	40	40	40	450	30	450	450	450	450	450	30	450	450	450	110	110	110	110
Pressure atm	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	19.74	19.74	19.74	19.74	19.74	19.74	19.74	19.74	19.74	19.74	1	1	1	1

B.4.: Mineral Acid pH-Swing Process

Table B- 9: Mass balance for mineral acid pH-swing process at 20% extraction and 65% carbonation

	PYROX	HCL	PYROX-FD	HCL-FD	PYR-REC	ACID-RE	SLURRY-1	PYR-SIO2	SIO2-PYR	LEACH-1	NAOH	LEACH-2	CO2	SOL-REC	SLURRY-2	ACID	SPENT-AC	ACID-REC	SLURRY-3	MGCO3	AQ-SOL	SOL-PRD
Substream: MIXED																						
Mole Flow kmol/hr				84	46																	
PYROXENE	42	0	42	0	74.7	0	93.3	93.3	18.7	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	21	0	21	0	35.7	10.1	0	0	10.1	0	0	0	0	42.0	42.0	6.3	35.7	0	0	0	0
MGCL2	0	0	0	0	0	0	23.3	0	0	23.3	0	23.3	0	13.1	15.4	0	0	0	15.4	0	15.4	2.3
SIO2	0	0	0	0	93.3	0	116.7	116.7	23.3	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	583.3	0	583.3	0	3415.9	4022.6	0	0	4022.6	74.1	4106.8	0	379.5	4465.3	4018.8	602.8	3415.9	446.5	0	446.5	67.0
NAOH	0	0	0	0	0	0	0	0	0	0	20	9.9	0	56.2	66.2	0	0	0	66.2	0	66.2	9.9
NACL	0	0	0	0	0	0	0	0	0	0	0	10.1	0	57.1	67.2	0	0	0	67.2	0	67.2	10.1
CO2	0	0	0	0	0	0	0	0	0	0	0	0	22.7	9.6	11.3	0	0	0	11.3	0	11.3	1.7
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	21.0	0	0	0	21.0	21.0	0	0
Mole Frac																						
PYROXENE	1	0	1	0	0.444	0	0.022	0.444	0.444	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.035	0	0.035	0	0.010	0.002	0	0	0.002	0	0	0	0	0.009	0.010	0.010	0.010	0	0	0	0
MGCL2	0	0	0	0	0	0	0.005	0	0	0.006	0	0.006	0	0.025	0.003	0	0	0	0.025	0	0.025	0.025
SIO2	0	0	0	0	0.556	0	0.027	0.556	0.556	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0.965	0	0.965	0	0.990	0.943	0	0	0.992	0.787	0.990	0	0.736	0.952	0.990	0.990	0.990	0.711	0	0.736	0.736
NAOH	0	0	0	0	0	0	0	0	0	0	0.213	0.002	0	0.109	0.014	0	0	0	0.105	0	0.109	0.109
NACL	0	0	0	0	0	0	0	0	0	0	0	0.002	0	0.111	0.014	0	0	0	0.107	0	0.111	0.111
CO2	0	0	0	0	0	0	0	0	0	0	0	0	1	0.019	0.002	0	0	0	0.018	0	0.019	0.019
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.004	0	0	0	0.033	1	0	0
Mass Flow kg/hr																						
PYROXENE	4216.3	0	4216.3	0	7495.7	0	9369.6	9369.6	1873.9	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	765.7	0	765.7	0	1303.1	367.3	0	0	367.3	0	0	0	0	1533.1	1533.1	230.0	1303.1	0	0	0	0
MGCL2	0	0	0	0	0	0	2221.6	0	0	2221.6	0	2221.6	0	1245.8	1465.7	0	0	0	1465.7	0	1465.7	219.9
SIO2	0	0	0	0	5607.9	0	7009.8	7009.8	1402.0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	10508.9	0	10508.9	0	61539.1	72468.4	0	0	72468.4	1334.5	73984.3	0	6837.7	80443.3	72398.9	10859.8	61539.1	8044.3	0	8044.3	1206.6
NAOH	0	0	0	0	0	0	0	0	0	0	799.9	397.0	0	2249.3	2646.2	0	0	0	2646.2	0	2646.2	396.9
NACL	0	0	0	0	0	0	0	0	0	0	0	588.8	0	3336.8	3925.7	0	0	0	3925.7	0	3925.7	588.9
CO2	0	0	0	0	0	0	0	0	0	0	0	0	1000	423.5	498.2	0	0	0	498.2	0	498.2	74.7
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1772.6	0	0	0	1772.6	1772.6	0	0
Mass Frac																						
PYROXENE	1	0	1	0	0.572	0	0.102	0.572	0.572	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.068	0	0.068	0	0.021	0.004	0	0	0.005	0	0	0	0	0.017	0.021	0.021	0.021	0	0	0	0
MGCL2	0	0	0	0	0	0	0.024	0	0	0.030	0	0.029	0	0.088	0.016	0	0	0	0.080	0	0.088	0.088
SIO2	0	0	0	0	0.428	0	0.077	0.428	0.428	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0.932	0	0.932	0	0.979	0.793	0	0	0.966	0.625	0.958	0	0.485	0.872	0.979	0.979	0.979	0.438	0	0.485	0.485
NAOH	0	0	0	0	0	0	0	0	0	0	0.375	0.005	0	0.160	0.029	0	0	0	0.144	0	0.160	0.160
NACL	0	0	0	0	0	0	0	0	0	0	0	0.008	0	0.237	0.043	0	0	0	0.214	0	0.237	0.237
CO2	0	0	0	0	0	0	0	0	0	0	0	0	1	0.030	0.005	0	0	0	0.027	0	0.030	0.030
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.019	0	0	0	0.097	1	0	0
Total Flow kmol/hr	42	604.3	42	604.3	168	3451.7	4266.0	210	42	4056.0	94.1	4150.1	22.7	515.6	4688.4	4060.8	609.1	3451.7	627.6	21.0	606.6	91.0
Total Flow kg/hr	4216.3	11274.6	4216.3	11274.6	13103.6	62842.2	91436.7	16379.5	3275.9	75057.3	2134.4	77191.7	1000	14093.1	92284.8	73932.0	11089.8	62842.2	18352.8	1772.6	16580.1	2487.0
Total Flow																						
Temperature C	25	25	70	70	70	70	70	70	70	70	25	25	30	20	20	20	20	20	20	20	20	20
Pressure atm	1	1	1	1	1	1	1	1	1	1	1	1	57.48	1	1	1	1	1	1	1	1	1

Table B- 10: Mass balance for mineral acid pH-swing process at 30% extraction and 90% carbonation

	PYROX	HCL	PYROX-FD	HCL-FD	PYR-REC	ACID-RE	SLURRY-1	PYR-SIO2	SIO2-PYR	LEACH-1	NAOH	LEACH-2	CO2	SOL-REC	SLURRY-2	ACID	SPENT-AC	ACID-REC	SLURRY-3	MGCO3	AQ-SOL	SOL-PRD
Substream: MIXED																						
Mole Flow kmol/hr																						
PYROXENE	42	0	42	0	53.5	0	66.8	66.8	13.4	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	33	0	33	0	38.0	13.7	0	0	13.7	0	0	0	0	44.7	44.7	6.7	38.0	0	0	0	0
MGCL2	0	0	0	0	0	0	28.6	0	0	28.6	0	28.6	0	35.6	41.9	0	0	0	41.9	0	41.9	6.3
SIO2	0	0	0	0	114.5	0	143.2	143.2	28.6	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	916.7	0	916.7	0	5154.8	6100.1	0	0	6100.1	74.1	6187.9	0	572.8	6738.3	6064.5	909.7	5154.8	673.8	0	673.8	101.1
NAOH	0	0	0	0	0	0	0	0	0	0	20	6.3	0	35.6	41.9	0	0	0	41.9	0	41.9	6.3
NACL	0	0	0	0	0	0	0	0	0	0	0	13.7	0	77.8	91.5	0	0	0	91.5	0	91.5	13.7
CO2	0	0	0	0	0	0	0	0	0	0	0	0	22.7	2.1	2.5	0	0	0	2.5	0	2.5	0.4
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.3	0	0	0	22.3	22.3	0	0
Mole Frac																						
PYROXENE	1	0	1	0	0.318	0	0.011	0.318	0.318	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.035	0	0.035	0	0.007	0.002	0	0	0.002	0	0	0	0	0.006	0.007	0.007	0.007	0	0	0	0
MGCL2	0	0	0	0	0	0	0.005	0	0	0.005	0	0.005	0	0.049	0.006	0	0	0	0.048	0	0.049	0.049
SIO2	0	0	0	0	0.682	0	0.023	0.682	0.682	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0.965	0	0.965	0	0.993	0.960	0	0	0.993	0.787	0.992	0	0.791	0.965	0.993	0.993	0.993	0.771	0	0.791	0.791
NAOH	0	0	0	0	0	0	0	0	0	0	0.213	0.001	0	0.049	0.006	0	0	0	0.048	0	0.049	0.049
NACL	0	0	0	0	0	0	0	0	0	0	0	0.002	0	0.107	0.013	0	0	0	0.105	0	0.107	0.107
CO2	0	0	0	0	0	0	0	0	0	0	0	0	1	0.003	0.000	0	0	0	0.003	0	0.003	0.003
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.003	0	0	0	0.026	1	0	0
Mass Flow kg/hr																						
PYROXENE	4216.3	0	4216.3	0	5366.2	0	6707.8	6707.8	1341.6	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	1203.2	0	1203.2	0	1385.3	500.3	0	0	500.3	0	0	0	0	1629.8	1629.8	244.5	1385.3	0	0	0	0
MGCL2	0	0	0	0	0	0	2726.5	0	0	2726.5	0	2726.5	0	3391.2	3989.6	0	0	0	3989.6	0	3989.6	598.4
SIO2	0	0	0	0	6882.4	0	8603.0	8603.0	1720.6	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	16514.0	0	16514.0	0	92865.4	109895.0	0	0	109895.0	1334.5	111477.0	0	10318.4	121393.0	109253.0	16388.0	92865.4	12139.3	0	12139.3	1820.9
NAOH	0	0	0	0	0	0	0	0	0	0	799.9	251.1	0	1423.2	1674.4	0	0	0	1674.4	0	1674.4	251.2
NACL	0	0	0	0	0	0	0	0	0	0	0	801.9	0	4543.9	5345.8	0	0	0	5345.8	0	5345.8	801.9
CO2	0	0	0	0	0	0	0	0	0	0	0	0	1000	92.9	109.3	0	0	0	109.3	0	109.3	16.4
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1884.4	0	0	0	1884.4	1884.4	0	0
Mass Frac																						
PYROXENE	1	0	1	0	0.438	0	0.052	0.438	0.438	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.068	0	0.068	0	0.015	0.004	0	0	0.004	0	0	0	0	0.012	0.015	0.015	0.015	0	0	0	0
MGCL2	0	0	0	0	0	0	0.021	0	0	0.024	0	0.024	0	0.172	0.029	0	0	0	0.159	0	0.172	0.172
SIO2	0	0	0	0	0.562	0	0.067	0.562	0.562	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0.932	0	0.932	0	0.985	0.856	0	0	0.971	0.625	0.967	0	0.522	0.892	0.985	0.985	0.985	0.483	0	0.522	0.522
NAOH	0	0	0	0	0	0	0	0	0	0	0.375	0.002	0	0.072	0.012	0	0	0	0.067	0	0.072	0.072
NACL	0	0	0	0	0	0	0	0	0	0	0	0.007	0	0.230	0.039	0	0	0	0.213	0	0.230	0.230
CO2	0	0	0	0	0	0	0	0	0	0	0	0	1	0.005	0.001	0	0	0	0.004	0	0.005	0.005
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.014	0	0	0	0.075	1	0	0
Total Flow kmol/hr	42	949.7	42	949.7	168	5192.8	6352.5	210	42	6142.5	94.1	6236.5	22.7	723.8	6983.1	6109.2	916.4	5192.8	873.9	22.3	851.6	127.7
Total Flow kg/hr	4216.3	17717.2	4216.3	17717.2	12248.6	94250.7	128433.0	15310.8	3062.2	113122	2134.4	115257	1000	19769.6	136026	110883.0	16632.5	94250.7	25142.8	1884.4	23258.4	3488.8
Total Flow																						
Temperature C	25	25	70	70	70	70	70	70	70	70	25	25	30	20	20	20	20	20	20	20	20	20
Pressure atm	1	1	1	1	1	1	1	1	1	1	1	1	57.48	1	1	1	1	1	1	1	1	1

Table B- 11: Mass balance for mineral acid pH-swing process at 30% extraction and 90% carbonation

	PYROX	HCL	PYROX-FD	HCL-FD	PYR-REC	ACID-RE	SLURRY-1	PYR-SIO2	SIO2-PYR	LEACH-1	NAOH	LEACH-2	CO2	SOL-REC	SLURRY-2	ACID	SPENT-AC	ACID-REC	SLURRY-3	MGCO3	AQ-SOL	SOL-PRD
Substream: MIXED																						
Mole Flow kmol/hr																						
PYROXENE	42	0	42	0	28	0	35	35	7	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	46	0	46	0	38.0	14.0	0	0	14.0	0	0	0	0	44.7	44.7	6.7	38.0	0	0	0	0
MGCL2	0	0	0	0	0	0	35	0	0	35	0	35	0	71.7	84.3	0	0	0	84.3	0	84.3	12.6
SIO2	0	0	0	0	140	0	175	175	35	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	1277.8	0	1277.8	0	7030.3	8343.1	0	0	8343.1	74.1	8431.2	0	781.1	9190.0	8271.0	1240.6	7030.3	919.0	0	919.0	137.8
NAOH	0	0	0	0	0	0	0	0	0	0	20	6.0	0	34.0	40.0	0	0	0	40.0	0	40.0	6.0
NACL	0	0	0	0	0	0	0	0	0	0	0	14.0	0	79.3	93.3	0	0	0	93.3	0	93.3	14.0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	22.7	2.1	2.5	0	0	0	2.5	0	2.5	0.4
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22.3	0	0	0	22.3	22.3	0	0
Mole Frac																						
PYROXENE	1	0	1	0	0.167	0	0.004	0.167	0.167	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.035	0	0.035	0	0.005	0.002	0	0	0.002	0	0	0	0	0.005	0.005	0.005	0.005	0	0	0	0
MGCL2	0	0	0	0	0	0	0.004	0	0	0.004	0	0.004	0	0.074	0.009	0	0	0	0.073	0	0.074	0.074
SIO2	0	0	0	0	0.833	0	0.020	0.833	0.833	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0.965	0	0.965	0	0.995	0.970	0	0	0.994	0.787	0.994	0	0.807	0.970	0.995	0.995	0.995	0.791	0	0.807	0.807
NAOH	0	0	0	0	0	0	0	0	0	0	0.213	0.001	0	0.035	0.004	0	0	0	0.034	0	0.035	0.035
NACL	0	0	0	0	0	0	0	0	0	0	0	0.002	0	0.082	0.010	0	0	0	0.080	0	0.082	0.082
CO2	0	0	0	0	0	0	0	0	0	0	0	0	1	0.002	0.000	0	0	0	0.002	0	0.002	0.002
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.002	0	0	0	0.019	1	0	0
Mass Flow kg/hr																						
PYROXENE	4216.3	0	4216.3	0	2810.9	0	3513.6	3513.6	702.7	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	1677.2	0	1677.2	0	1385.3	510.2	0	0	510.2	0	0	0	0	1629.8	1629.8	244.5	1385.3	0	0	0	0
MGCL2	0	0	0	0	0	0	3332.4	0	0	3332.4	0	3332.4	0	6824.6	8029.0	0	0	0	8029.0	0	8029.0	1204.3
SIO2	0	0	0	0	8411.8	0	10514.8	10514.8	2103.0	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	23019.5	0	23019.5	0	126653	150303	0	0	150303	1334.5	151890	0	14072.6	165560.0	149004	22350.6	126653	16556.0	0	16556.0	2483.4
NAOH	0	0	0	0	0	0	0	0	0	0	799.9	240.2	0	1360.4	1600.5	0	0	0	1600.5	0	1600.5	240.1
NACL	0	0	0	0	0	0	0	0	0	0	0	817.9	0	4634.1	5451.9	0	0	0	5451.9	0	5451.9	817.8
CO2	0	0	0	0	0	0	0	0	0	0	0	0	1000	92.9	109.3	0	0	0	109.3	0	109.3	16.4
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1884.4	0	0	0	1884.4	1884.4	0	0
Mass Frac																						
PYROXENE	1	0	1	0	0.250	0	0.021	0.250	0.250	0	0	0	0	0	0	0	0	0	0	0	0	0
HCL	0	0.068	0	0.068	0	0.011	0.003	0	0	0.003	0	0	0	0	0.009	0.011	0.011	0.011	0	0	0	0
MGCL2	0	0	0	0	0	0	0.020	0	0	0.022	0	0.021	0	0.253	0.044	0	0	0	0.239	0	0.253	0.253
SIO2	0	0	0	0	0.750	0	0.063	0.750	0.750	0	0	0	0	0	0	0	0	0	0	0	0	0
WATER	0	0.932	0	0.932	0	0.989	0.894	0	0	0.975	0.625	0.972	0	0.522	0.898	0.989	0.989	0.989	0.492	0	0.522	0.522
NAOH	0	0	0	0	0	0	0	0	0	0	0.375	0.002	0	0.050	0.009	0	0	0	0.048	0	0.050	0.050
NACL	0	0	0	0	0	0	0	0	0	0	0	0.005	0	0.172	0.030	0	0	0	0.162	0	0.172	0.172
CO2	0	0	0	0	0	0	0	0	0	0	0	0	1	0.003	0.001	0	0	0	0.003	0	0.003	0.003
MGCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.010	0	0	0	0.056	1	0	0
Total Flow kmol/hr	42	1323.8	42	1323.8	168.0	7068.3	8602.1	210	42	8392.1	94.1	8486.2	22.7	968.2	9477.1	8315.7	1247.4	7068.3	1161.5	22.3	1139.1	170.9
Total Flow kg/hr	4216.3	24696.7	4216.3	24696.7	11222.7	128039.0	168174.0	14028.4	2805.7	154146	2134.4	156280	1000	26984.7	184265	150634	22595.1	128039	33631.1	1884.4	31746.7	4762.0
Total Flow																						
Temperature C	25	25	70	70	70	70	70	70	70	70	25	25	30	20	20	20	20	20	20	20	20	20
Pressure atm	1	1	1	1	1	1	1	1	1	1	1	1	57.48	1	1	1	1	1	1	1	1	1

B.5.: Direct Aqueous Carbonation Process

Table B- 12: Mass balance for direct aqueous carbonation process at 5% carbonation

	H2O	CO2	H2O-	CO2-	H2O-CO2	PYROX	PYROX-FD	PYR-REC	SOL-REC	SLURRY	SOLN	SPNT-SOL	SOLIDS	SIO2-PYR	MGCO3	PYR-SIO2
Substream: MIXED																
Mole Flow kmol/hr																
PYROX	0	0	0	0	0	86	86	360.8	0	424.4	0	0	424.4	424.4	0	63.7
WATER	998.3	0	998.3	0	975.5	0	0	0	18958	19955.8	19955.8	997.8	0	0	0	0
CO2	0	22.7	0	22.7	0	0	0	0	0	0	0	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	22.3	0	0	22.3	0	22.3	0
SIO2	0	0	0	0	0	0	0	126.6	0	148.9	0	0	148.9	148.9	0	22.3
H2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NAHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NACL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H+	0	0	0	0	22.7	0	0	0	7.3	7.7	7.7	0.4	0	0	0	0
NA+	29.5	0	29.5	0	29.5	0	0	0	559.9	589.3	589.3	29.5	0	0	0	0
OH-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CL-	18.0	0	18.0	0	18.0	0	0	0	341.4	359.3	359.3	18.0	0	0	0	0
HCO3-	11.5	0	11.5	0	34.2	0	0	0	225.8	237.7	237.7	11.9	0	0	0	0
Mass Flow kg/hr																
PYROX	0	0	0	0	0	8633.4	8633.4	36215.6	0	42606.5	0	0	42606.5	42606.5	0	6391.0
WATER	17984	0	17984	0	17574.7	0	0	0	341534	359509	359509	17975.5	0	0	0	0
CO2	0	1000	0	1000	0	0	0	0	0	0	0	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	1883.4	0	0	1883.4	0	1883.4	0
SIO2	0	0	0	0	0	0	0	7605.5	0	8947.6	0	0	8947.6	8947.6	0	1342.1
H2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NAHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NACL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H+	0	0	0	0	22.9	0	0	0	7.4	7.8	7.8	0.4	0	0	0	0
NA+	677.5	0	677.5	0	677.5	0	0	0	12870.7	13548.1	13548.1	677.4	0	0	0	0
OH-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CL-	637.1	0	637.1	0	637.1	0	0	0	12102.9	12739.9	12739.9	637.0	0	0	0	0
HCO3-	701.7	0	701.7	0	2088.2	0	0	0	13777.7	14502.9	14502.9	725.1	0	0	0	0
Total Flow kmol/hr	1057.2	22.7	1057.2	22.7	1079.9	86	86	487.3	20092.4	21745.5	21149.8	1057.5	595.7	573.3	22.3	86
Total Flow kg/hr	20000.2	1000	20000.2	1000	21000.2	8633.4	8633.4	43821.0	380292	453745	400308	20015.4	53437.5	51554.2	1883.4	7733.1
Total Flow cum/hr	18.7	1.6	20.9	2.1	21.4	2.6	2.6	13.7	397.7	435.4	418.7	20.9	16.7	16.1	0.6	2.4
Temperature C	25	30	185	185	185	25	185	184.9805	184.9805	185	184.9805	184.9805	184.9805	184.9805	184.9805	184.9805
Pressure atm	1	150	150	150	150	1	1	150	150	150	150	150	150	150	150	150

Table B- 13: Mass balance for direct aqueous carbonation process at 20% carbonation

	H2O	CO2	H2O-	CO2-	H2O-CO2	PYROX	PYROX-FD	PYR-REC	SOL-REC	SLURRY	SOLN	SPNT-SOL	SOLIDS	SIO2-PYR	MGCO3	PYR-SIO2
Substream: MIXED																
Mole Flow kmol/hr																
PYROX	0	0	0	0	0	30	30	77.1	0	85.7	0	0	85.7	85.7	0	8.6
WATER	434.0	0	434.0	0	411.3	0	0	0	8221.2	8653.9	8653.9	432.7	0	0	0	0
CO2	0	22.7	0	22.7	0	0	0	0	0	0	0	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	21.4	0	0	21.4	0	21.4	0
SIO2	0	0	0	0	0	0	0	192.9	0	214.3	0	0	214.3	214.3	0	21.4
H2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NAHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NACL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H+	0	0	0	0	22.7	0	0	0	24.6	25.9	25.9	1.3	0	0	0	0
NA+	13	0	13	0	13	0	0	0	247.0	260.0	260.0	13.0	0	0	0	0
OH-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CL-	8	0	8	0	8	0	0	0	152.0	160.0	160.0	8.0	0	0	0	0
HCO3-	5	0	5	0	27.7	0	0	0	119.6	125.9	125.9	6.3	0	0	0	0
Mass Flow kg/hr																
PYROX	0	0	0	0	0	3011.7	3011.7	7744.3	0	8604.7	0	0	8604.7	8604.7	0	860.5
WATER	7819.1	0	7819.1	0	7409.8	0	0	0	148107	155902	155902	7795.122	0	0	0	0
CO2	0	1000	0	1000	0	0	0	0	0	0	0	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	1806.7	0	0	1806.7	0	1806.7	0
SIO2	0	0	0	0	0	0	0	11587.7	0	12875.2	0	0	12875.2	12875.2	0	1287.5
H2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NAHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NACL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H+	0	0	0	0	22.9	0	0	0	24.8	26.1	26.1	1.3	0	0	0	0
NA+	298.9	0	298.9	0	298.9	0	0	0	5677.8	5976.7	5976.7	298.8	0	0	0	0
OH-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CL-	283.6	0	283.6	0	283.6	0	0	0	5388.4	5672	5672	283.6	0	0	0	0
HCO3-	305.1	0	305.1	0	1691.5	0	0	0	7296.1	7680.1	7680.1	384	0	0	0	0
Total Flow kmol/hr	460	22.7	460	22.7	482.8	30	30	270	8764.3	9547	9225.6	461.3	321.4	300	21.4	30
Total Flow kg/hr	8706.7	1000	8706.7	1000	9706.7	3011.7	3011.7	19332	166494	198544	175257	8762.9	23286.7	21480	1806.7	2148
Total Flow cum/hr	8.1	1.6	9.1	2.1	9.5	0.9	0.9	6.7	173.5	190.7	182.6	9.1	8.0	7.4	0.6	0.7
Temperature C	25	30	185	185	185	25	185	185	185	185	185	185	185	185	185	185
Pressure atm	1	150	150	150	150	1	1	150	150	150	150	150	150	150	150	150

Unit Energy Balances for Carbonation Processes

C.1: Ammonium Salts Process

Table C-1: Mineral dissolution unit energy balance for 30% extraction

	PYROX	NH4HSO4	PYROX-FD	BISUL-FD	PYR-REC	BIS-REC	SLURRY
Substream: MIXED							
Mole Flow kmol/hr							
PYROX	22.70	0	22.70	0	28.89	0	36.11
NH4HSO4	0	0	0	0	0	0	0
MGSO4	0	0	0	0	0	0	0
SIO2	0	0	0	0	61.91	0	77.39
NH4SO4	0	0	0	0	0	0	0
WATER	0	357.14	0	357.14	0	1 143.07	1 515.69
NH4OH	0	0	0	0	0	0	0
NH4HCO3	0	0	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0
NH3	0	0	0	0	0	0	0
MG++	0	0	0	0	0	1.35	16.83
H3O+	0	1.982E-06	0	1.05E-05	0	2.5E-10	2.63E-10
NH4+	0	9.00	0	9.00	0	74.17	83.17
H2SO4	0	3.04E-16	0	5.71E-13	0	7.13E-18	2.99E-18
OH-	0	1.982E-06	0	1.05E-05	0	9.20	9.20
HSO4-	0	9.00	0	9.00	0	34.65	12.70
HCO3-	0	0	0	0	0	30.32	30.32
CO3--	0	0	0	0	0	0	0
SO4--	0	0	0	0	0	1.35	32.30
Total Flow kmol/hr	22.70	375.14	22.70	375.14	90.80	1 294.11	1 813.70
Total Flow kg/hr	2 278.82	7 469.97	2 278.82	7 469.97	6 620.05	27 463.18	43 832.01
Total Flow cum/hr	0.681	7.49	0.681	7.73	2.27	27.08	35.24
Temperature C	25.00	25.00	90.00	90.00	90.00	90.00	90.00
Pressure atm	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Vapor Frac	0	0	0	0	0	0	0
Liquid Frac	0	1.00	0	1.00	0	1.00	0.937421
Solid Frac	1.00	0	1.00	0	1.00	0	0.062579
Enthalpy kJ/kmol	-1548900	-296720	-1543300	-292020	-1109900	-298640	-349700
Enthalpy kJ/kg	-15429.2	-14901.32	-15373.11	-14665.2	-15222.6	-14072.5	-14469.9
Enthalpy kW	-9766.78	-30920.1	-9731.282	-30430	-27992.9	-107350	-176180
Entropy J/kmol-K	-291450	-169650	-274390	-155380	-205320	-161560	-162890
Entropy J/kg-K	-2903.2	-8519.738	-2733.321	-7803.29	-2816.13	-7613.02	-6740.2
Density kmol/cum	33.33	50.11	33.33	48.50	39.98	47.78	51.47
Density kg/cum	3 346.29	997.87	3 346.29	965.81	2 914.63	1 014.00	1 243.98
Average MW	100.39	19.91	100.39	19.91	72.91	21.22	24.17
Liq Vol 60F							

Table C-2: pH adjustment unit energy balance for 30% extraction

	LEACH-1	LEACH-2	NH4OH	LEACH-3
Substream: MIXED				
Mole Flow kmol/hr				
PYROX	0	0	0	0
NH4HSO4	0	0	0	0
MGSO4	0	0	0	0
SIO2	0	0	0	0
NH4SO4	0	0	0	0
WATER	1 515.71	1 515.71	416.67	1 945.08
NH4OH	0	0	0	0
NH4HCO3	0	0	0	0
MGCO3	0	0	0	0
CO2	0	0	0	0
NH3	0	0	0	0
MG++	16.82	16.82	0	16.82
H3O+	2.63E-10	5.97E-12	1.08E-13	6.06E-12
NH4+	83.18	83.18	15.00	98.18
H2SO4	2.99E-18	2.99E-22	0	0
OH-	9.20	9.20	15.00	11.50
HSO4-	12.70	12.70	0	0
HCO3-	30.32	30.32	0	30.32
CO3--	0	0	0	0
SO4--	32.30	32.30	0	45.00
Total Flow kmol/hr	1 700.23	1 700.23	446.67	2 146.90
Total Flow kg/hr	35 557.36	35 557.36	8 032.11	43 589.48
Total Flow cum/hr	32.40	31.36	7.79	38.48
Temperature C	90.00	25.00	25.00	25.00
Pressure atm	1.00	1.00	1.00	1.00
Vapor Frac	0	0	0	0
Liquid Frac	1.00	1.00	1.00	1.00
Solid Frac	0	0	0	0
Enthalpy kJ/kmol	-298950	-303390	-278930	-298750
Enthalpy kJ/kg	-14294.7	-14507.1	-15511.3	-14714.4
Enthalpy kW	-141190	-143290	-34607.9	-178160
Entropy J/kmol-K	-160060	-173530	-165800	-171990
Entropy J/kg-K	-7653.48	-8297.56	-9220.29	-8471.19
Density kmol/cum	52.48	54.22	57.37	55.80
Density kg/cum	1 097.54	1 133.97	1 031.56	1 132.84
Average MW	20.91	20.91	17.98	20.30

Table C-3: Mineral carbonation unit energy balance for 30% extraction

	LEACH-3	NH4-HCO3	CARB-FD	NH4HCO3-	CARB-PRD
Substream: MIXED					
Mole Flow kmol/hr					
PYROX	0	0	0	0	0
NH4HSO4	0	0	0	0	0
MGSO4	0	0	0	0	0
SIO2	0	0	0	0	0
NH4SO4	0	0	0	0	0
WATER	1 945.07	117.69	1 945.07	117.69	2 032.48
NH4OH	0	0	0	0	0
NH4HCO3	0	0	0	0	0
MGCO3	0	0	0	0	15.14
CO2	0	0	0	0	15.14
NH3	0	0	0	0	0
MG++	16.82	0	16.82	0	1.68
H3O+	6.064E-12	8.5411E-07	1.849E-10	9.0605E-06	2.2962E-10
NH4+	98.18	37.86	98.18	37.86	136.04
OH-	11.50	8.5411E-07	11.50	9.0605E-06	11.50
HSO4-	0	0	0	0	0
HCO3-	30.32	37.86	30.32	37.86	37.90
SO4--	45.00	0	45.00	0	45.00
Total Flow kmol/hr	2 146.89	193.41	2 146.89	193.41	2 294.89
Total Flow kg/hr	43 589.30	5 113.27	43 589.30	5 113.27	48 702.56
Total Flow cum/hr	38.48	3.92	39.49	4.04	813.44
Temperature C	25.00	10.00	80.00	80.00	80.00
Pressure atm	1.00	1.00	1.00	1.00	1.00
Vapor Frac	0	0	0	0	0.0116367
Liquid Frac	1.00	1.00	1.00	1.00	0.9817669
Solid Frac	0	0	0	0	0.00659641
Enthalpy kJ/kmol	-298750	-336060	-294980	-331260	-303580
Enthalpy kJ/kg	-14714.36	-12711.35	-14528.45	-12529.79	-14305.03
Enthalpy kW	-178160	-18054.58	-175910	-17796.7	-193530
Entropy J/kmol-K	-171990	-205240	-160380	-190110	-165010
Entropy J/kg-K	-8471.188	-7763.247	-7899.142	-7190.825	-7775.24
Density kmol/cum	55.80	49.31	54.37	47.93	2.82
Density kg/cum	1 132.84	1 303.71	1 103.87	1 267.03	59.87
Average MW	20.30	26.44	20.30	26.44	21.22

Table C-4: CO_2 capture unit energy balance for 30% extraction

	CO2-IN	CO2-	CAP-H2O	CAP-NH3	NH4HCO3
Substream: MIXED					
Mole Flow kmol/hr					
PYROX	0	0	0	0	0
NH4HSO4	0	0	0	0	0
MGSO4	0	0	0	0	0
SIO2	0	0	0	0	0
NH4SO4	0	0	0	0	0
WATER	0	0	603.65	0	565.79
NH4OH	0	0	0	0	0
NH4HCO3	0	0	0	0	0
MGCO3	0	0	0	0	0
CO2	22.72	15.14	0	0	0
NH3	0	0	0	43.32	5.46
MG++	0	0	0	0	0
H3O+	0	0	5.896E-07	0	0.000939472
NH4+	0	0	0	0	37.86
OH-	0	0	5.896E-07	0	5.2051E-09
HSO4-	0	0	0	0	0
HCO3-	0	0	0	0	37.86
CO3--	0	0	0	0	0.000939467
SO4--	0	0	0	0	0
Total Flow kmol/hr	22.72	15.14	603.65	43.32	646.97
Total Flow kg/hr	999.90	666.31	10 874.92	737.76	13 278.90
Total Flow cum/hr	524.84	349.74	10.88	1 285.45	12.05
Temperature C	10.00	10.00	10.00	90.00	10.00
Pressure atm	1.00	1.00	1.00	1.00	1.00
Vapor Frac	1.00	1.00	0	1.00	0
Liquid Frac	0	0	1.00	0	1.00
Solid Frac	0	0	0	0	0
Enthalpy kJ/kmol	-394360	-394360	-287140	-43374.32	-300050
Enthalpy kJ/kg	-8960.72	-8960.723	-15938.58	-2546.852	-14618.82
Enthalpy kW	-2488.85	-1658.501	-48147.47	-521.9376	-53922.73
Entropy J/kmol-K	959.37	959.37	-167490	-91985.67	-178360
Entropy J/kg-K	21.80	21.80	-9296.992	-5401.212	-8689.797
Density kmol/cum	0.04329	0.0432897	55.50	0.0337003	53.71
Density kg/cum	1.91	1.91	999.80	0.5739354	1 102.40
Average MW	44.01	44.01	18.02	17.03	20.52

Table C-5: Thermal decomposition (EVAP) unit energy balance for 30% extraction

	DEC-FD	DEC-PRD
Substream: MIXED		
Mole Flow kmol/hr		
PYROX	0	0
NH4HSO4	0	43.32
MGSO4	0	0
SIO2	0	0
NH4SO4	43.32	0
WATER	20.32	20.32
NH4OH	0	0
NH4HCO3	0	0
MGCO3	0	0
CO2	0	0
NH3	0	43.32
MG++	1.68	1.68
H3O+	8.38E-15	8.34E-16
NH4+	49.40	49.40
H2SO4	0	0
HSO4-	1.1E-11	3.46E-12
OH-	11.50	11.50
HCO3-	37.90	37.90
CO3--	0	0
SO4--	1.68	1.68
Total Flow kmol/hr	165.80	209.12
Total Flow kg/hr	9 691.86	9 691.86
Total Flow kcum/hr	0.938905	2.99
Temperature C	300.00	300.00
Pressure atm	1.00	1.00
Vapor Frac	0.119859	0.303341
Liquid Frac	0.618862	0.489506
Solid Frac	0.261279	0.207154
Enthalpy kJ/kmol	-519090	-388130
Enthalpy kJ/kg	-8880.07	-8374.59
Enthalpy kW	-23906.8	-22545.9
Entropy J/kmol-K	-308780	-781040
Entropy J/kg-K	-5282.35	-16852.5
Density kmol/cum	0.176589	0.070028
Density kg/cum	10.32	3.25
Average MW	58.46	46.35

Table C-6: Mineral carbonation unit energy balance for 90% dissolution

	LEACH-3	NH4-HCO3	CARB-FD	NH4HCO3-	WATER	CARB-PRD
Substream: MIXED						
Mole Flow kmol/hr						
PYROX	0	0	0	0	0	0
NH4HSO4	0	0	0	0	0	0
MGSO4	0	0	0	0	0	0
SIO2	0	0	0	0	0	0
NH4SO4	0	0	0	0	0	0
WATER	27.80	2.07	27.80	2.07	67	54.80
NH4OH	3.16	0	3.16	0	0	3.16
NH4HCO3	0	0	0	0	0	0
MGCO3	0	0	0	0	0	21.04
CO2	0	0	0	0	0	21.04
NH3	0.0003	2.50E-06	0.005	4.07E-05	0	0.013
MG++	23.38	0	23.38	0	0	2.34
H3O+	1.32E-06	2.50E-06	6.31E-06	4.07E-05	1.21E-07	5.45E-05
NH4+	54.93	43.76	54.93	43.76	0	98.68
OH-	6.38E-10	7.06E-11	4.49E-09	5.11E-10	1.21E-07	3.49E-09
HSO4-	0.0003	0	0.005	0	0	0.013
HCO3-	1.68	43.76	1.68	43.76	0	3.36
CO3--	0	0	0	0	0	0
SO4--	50.00	0	49.99	0	0	49.99
Total Flow kmol/hr	160.96	89.58	160.96	89.58	67	254.43
Total Flow kg/hr	7076.61	3496.55	7076.61	3496.55	1207.02	11780.19
Total Flow cum/hr	2.82	2.26	2.97	2.33	1.21	686.34
Temperature C	25	10	80	80	25	80
Pressure atm	1	1	1	1	1	1
Vapor Frac	0	0	0	0	0	0.093
Liquid Frac	1	1	1	1	1	0.825
Solid Frac	0	0	0	0	0	0.083
Enthalpy kJ/kmol	-449930	-409070	-448600	-404680	-286010	-499490
Enthalpy kJ/kg	-10233.5	-10480.47	-10203.43	-10368.1	-15875.82	-10787.96
Enthalpy kW	-20116.27	-10179.31	-20057.15	-10070.17	-5322.916	-35301.16
Entropy J/kmol-K	-234640	-263730	-230310	-249930	-163360	-266060
Entropy J/kg-K	-5336.96	-6756.95	-5238.33	-6403.27	-9067.981	-5746.29
Density kmol/cum	57.16	39.60	54.15	38.48	55.35	0.37
Density kg/cum	2513.08	1545.54	2380.79	1502.04	997.17	17.16
Average MW	43.97	39.03	43.97	39.03	18.02	46.30

C.2. Lackner's HCl Multi-stage Process

Table C-7: Mineral dissolution unit energy balance for 30% extraction

	PYROX	HCL	PYROX-FD	HCL-FD	PYR-REC	HCL-REC	SLURRY-1
Substream: MIXED							
Mole Flow kmol/hr							
PYROX	56.1	0	56.1	0	95.52	0	106.134
HCL	0	0	0	0	0	0	0
WATER	0	1391.67	0	1391.67	0	3578.57	4742.81
MGCL2-W	0	0	0	0	0	0	45.49
SIO2	0	0	0	0	409.37	0	454.86
MGOHCL	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0
MGCL2	0	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0
MG++	0	0	0	0	0	0	0
H+	0	50.1	0	50.1	0	41.52	0.648
OH-	0	3.29E-13	0	4.40E-12	0	4.31E-11	2.17E-09
HCO3-	0	0	0	0	0	0	0
CL-	0	50.1	0	50.1	0	41.52	0.648
CO3--	0	0	0	0	0	0	0
Mole Frac							
PYROX	1	0	1	0	0.189	0	0.020
HCL	0	0	0	0	0	0	0
WATER	0	0.933	0	0.933	0	0.977	0.886
MGCL2-W	0	0	0	0	0	0	0.009
SIO2	0	0	0	0	0.811	0	0.085
MGOHCL	0	0	0	0	0	0	0
MGOH	0	0	0	0	0	0	0
MGCL2	0	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0
MG++	0	0	0	0	0	0	0
H+	0	0.034	0	0.034	0	0.011	0.000
OH-	0	2.20E-16	0	2.95E-15	0	1.18E-14	4.06E-13
HCO3-	0	0	0	0	0	0	0
CL-	0	0.034	0	0.034	0	0.011	0.000
CO3--	0	0	0	0	0	0	0
Total Flow kmol/hr	56.1	1491.87	56.1	1491.87	504.89	3661.61	5350.58
Total Flow kg/hr	5631.81	26898	5631.81	26898	34185.84	65982.79	132698
Total Flow cum/hr	1.68	26.98	1.683	27.52	12.15	67.46	104.52
Temperature C	25	25	70	70	70	70	70
Pressure atm	1	1	1	1	1	1	1
Vapor Frac	0	0	0	0	0	0	0
Liquid Frac	0	1	0	1	0	1	0.887
Solid Frac	1	0	1	0	1	0	0.113
Enthalpy kJ/kmol	-1548900	-272500	-1545100	-269440	-1029000	-278170	-379550
Enthalpy kJ/kg	-15429.2	-15113.86	-15390.95	-14944.09	-15197.37	-15436.42	-15303.84
Enthalpy kW	-24137.29	-112930	-24077.46	-111660	-144320	-282930	-564110
Entropy J/kmol-K	-291450	-156090	-279470	-146530	-195500	-150330	-166330
Entropy J/kg-K	-2903.20	-8657.55	-2783.83	-8127.22	-2887.37	-8342.58	-6706.67
Density kmol/cum	33.33	55.30	33.33	54.22	41.54	54.28	51.19
Density kg/cum	3346.29	997.01	3346.29	977.54	2812.87	978.14	1269.62
Average MW	100.39	18.03	100.39	18.03	67.71	18.02	24.80

Table C-8: Conversion and repartition unit energy balance for 30% extraction

	Conversion		Repartition	
	MGCL2-W	**MGOHCL-H**	**MGOHCL**	**SLURRY-2**
Substream: MIXED				
Mole Flow kmol/hr			0	0
MGSIO3	0	0	0	0
HCL	0	0	994.05	994.05
WATER	4742.81	4970.26	0	0
MGCL2-W	45.49	0	0	0
SIO2	0	0	45.49	0
MGOHCL	0	45.49	0	22.75
MGOH	0	0	0	0
MGCL2	0	0	0	0
CO2	0	0	0	0
MGCO3	0	0	0	22.75
MG++	0	0	7.12E-06	4.78E-06
H+	0.649	46.139	7.12E-06	4.78E-06
OH-	2.17E-09	6.70E-15	0	45.49
CL-	0.649	46.14	1039.54	1085.03
Total Flow kmol/hr	4789.60	5108.03	21400.13	21400.13
Total Flow kg/hr	94714.92	94714.92	19.68	19.27
Total Flow cum/hr	91.01	167803	70	70
Temperature C	70	150	1	1
Pressure atm	1	1	0	0
Vapor Frac	0	0.951	0.956	0.979
Liquid Frac	0.991	0.040	0.044	0.021
Solid Frac	0.009	0.009	-305090	-295280
Enthalpy kJ/kmol	-303480	-240540	-14820.2	-14971.27
Enthalpy kJ/kg	-15346.51	-12972.19	-88098.38	-88996.45
Enthalpy kW	-403760	-341290	-155430	-151770
Entropy J/kmol-K	-162910	-37015.43	-7550.30	-7694.89
Entropy J/kg-K	-8238.35	-1996.26	52.82	56.30
Density kmol/cum	52.62	0.030	1087.34	1110.34
Density kg/cum	1040.65	0.564	20.59	19.72
Average MW	19.78	18.54		
Liq Vol 60F				

Table C-9: Mineral carbonation unit energy balance for 30% extraction

	CO2	MGOH	MGOH-H2
Substream: MIXED			
Mole Flow kmol/hr			
MGSIO3	0	0	0
HCL	0	0	0
WATER	0	0	22.72
MGCL2-W	0	0	0
SIO2	0	0	0
MGOHCL	0	0	0
MGOH	0	22.74	0.02
MGCL2	0	0	0
CO2	22.72	0	0
MGCO3	0	0	22.72
Total Flow kmol/hr	22.72	22.74	45.46
Total Flow kg/hr	999.90	1326.19	2326.09
Total Flow cum/hr	5.84	0.560	1266.65
Temperature C	25	70	406.85
Pressure atm	57.48	1	1
Vapor Frac	1	0	0.500
Liquid Frac	0	0	0
Solid Frac	0	1	0.500
Enthalpy kJ/kmol	-396560	-920870	-652300
Enthalpy kJ/kg	-9010.61	-15790.09	-12748.2
Enthalpy kW	-2502.704	-5816.85	-8237.08
Entropy J/kmol-K	-38314.09	-293890	-109110
Entropy J/kg-K	-870.58	-5039.27	-2132.35
Density kmol/cum	3.89	40.60	0.036
Density kg/cum	171.07	2367.83	1.84
Average MW	44.01	58.32	51.17
Liq Vol 60F cum/hr	1.22		

C.3. Åbo Akademi University (AAU) Process

Table C-10: Mg-extraction (AS-REAC) unit energy balance for 66% extraction and 55% carbonation

	A-SULF	PYROX	PYROX-FD	PYR-REC	AS-REC	ASR-PRD
Substream: MIXED						
Mole Flow kmol/hr						
PYROX	0	25.5	25.5	11.24	0	12.49
SULFATE	3	0	0	0	27.00	5.75
MGSO4	0	0	0	0	0	24.25
SIO2	0	0	0	218.08	0	242.33
NH3	0	0	0	0	0	48.4968
WATER	0	0	0	0	0	24.25
MGOH	0	0	0	0	0	0
CO2	0	0	0	0	0	0
MGCO3	0	0	0	0	0	0
Total Flow kmol/hr	3	25.5	25.5	229.32	27.00	357.57
Total Flow kg/hr	396.42	2559.91	2559.91	14231.55	3567.796	20755.68
Total Flow cum/hr	0.224	0.765	0.765	5.29	2.03	4025.60
Temperature C	25	25	400	40	110	400
Pressure atm	1	1	1	1	1	1
Vapor Frac	0	0	0	0	0	0.203
Liquid Frac	0	0	0	0	0	0
Solid Frac	1	1	1	1	1	0.797
Enthalpy kJ/kmol	-1180900	-1548900	-1511700	-941270	-1163900	-776830
Enthalpy kJ/kg	-8936.315	-15429.2	-15058.18	-15167.2	-8807.85	-13382.7
Enthalpy MJ/hr	-3542.55	-39497.38	-38547.61	-215850	-31424.6	-277770
Entropy J/kmol-K	-936350	-291450	-212070	-185520	-886380	-407610
Entropy J/kg-K	-7086.02	-2903.204	-2112.46	-2989.32	-6707.86	-7021.98
Density kmol/cum	13.41	33.33	33.33	43.37	13.29	0.089
Density kg/cum	1772.402	3346.29	3346.29	2691.47	1755.94	5.16
Average MW	132.14	100.39	100.39	62.06	132.14	58.05
Liq Vol 60F						

Table C-11: Precipitation unit energy balance for 66% extraction and 55% carbonation

	NH3-H2O	NH3-H2O-	MGSO-4	SLURRY-2
Substream: MIXED				
Mole Flow kmol/hr				
PYROX	0	0	0	0
SULFATE	0	0	0	0
MGSO4	0	0	0	0
SIO2	0	0	0	0
NH3	48.5	48.5	0	0
WATER	24.25	24.25	47.08	22.83
MGOH	0	0	0	24.25
CO2	0	0	0	0
MGCO3	0	0	0	0
MG++	0	0	24.25	0
H3O+	0	1.34E-09	1.42E-07	7.26E-08
NH4+	0	0	11.50	60.00
HCO3-	0	0	0	0
OH-	0	1.34E-09	1.42E-07	7.26E-08
CO3--	0	0	0	0
SO4--	0	0	30.00	30.00
Total Flow kmol/hr	72.75	72.75	112.83	137.08
Total Flow kg/hr	1262.85	1262.85	4526.906	5789.76
Total Flow cum/hr	4014.98	957.35	1.11	3.19
Temperature C	400	25	40	40
Pressure atm	1	1	1	1
Vapor Frac	1	0.541	0	0
Liquid Frac	0	0.459	1	0.823
Solid Frac	0	0	0	0.177
Enthalpy kJ/kmol	-96373.39	-129260	-471870	-466030
Enthalpy kJ/kg	-5551.85	-7446.08	-11761.14	-11033.88
Enthalpy MJ/hr	-7011.164	-9403.30	-53241.57	-63883.49
Entropy J/kmol-K	-43992.3	-130240	-227600	-277180
Entropy J/kg-K	-2534.29	-7503.09	-5672.70	-6562.69
Density kmol/cum	0.018	0.076	101.77	42.92
Density kg/cum	0.314535	1.32	4083.27	1812.58
Average MW	17.36	17.36	40.12	42.24
Liq Vol 60F cum/hr	3.04			

Table C-12: Mineral carbonation unit energy balance for 66% extraction and 55% carbonation

	MGOH	CO2	MGOH-	CARB-REC	MGCO-H2
Substream: MIXED					
Mole Flow kmol/hr					
PYROX	0	0	0	0	0
SULFATE	0	0	0	0	0
MGSO4	0	0	0	0	0
SIO2	0	0	0	0	0
NH3	0	0	0	0	0
WATER	0	0	0	0	22.42
MGOH	24.25	0	24.25	16.51	18.34
CO2	0	22.72	0	2.75	3.05
MGCO3	0	0	0	0	22.42
Total Flow kmol/hr	24.25	22.72221	24.25	19.26	66.23
Total Flow kg/hr	1414.25	1000.00	1414.25	1083.89	3498.14
Total Flow cum/hr	0.597	555.90	0.597	8.67	77.66
Temperature C	40	25	450	450	450
Pressure atm	1	1	1	19.74	19.74
Vapor Frac	0	1	0	0.143	0.385
Liquid Frac	0	0	0	0	0
Solid Frac	1	0	1	0.857	0.615
Enthalpy kJ/kmol	-923360	-393510	-882980	-810390	-701080
Enthalpy kJ/kg	-15832.7	-8941.418	-15140.29	-14400.1	-13274.01
Enthalpy MJ/hr	-22391.43	-8941.417	-21412.19	-15608.05	-46434.29
Entropy J/kmol-K	-301460	2884.454	-220560	-186680	-138190
Entropy J/kg-K	-5169.128	65.54118	-3781.892	-3317.116	-2616.453
Density kmol/cum	40.60089	0.0408747	40.60089	2.22047	0.8528946
Density kg/cum	2367.831	1.798887	2367.831	124.9602	45.04669
Average MW	58.31968	44.0098	58.31968	56.27647	52.81625
Liq Vol 60F		1.216952			

C.4. Mineral Acid pH-Swing Process

Table C-13: Mineral dissolution unit energy balance for 20% extraction and 65% carbonation

	PYROX	HCL	ACID-REC	PYROX-FD	HCL-FD	ACID-RE	PYR-REC	SLURRY-1
Substream: MIXED								
Mole Flow kmol/hr								
PYROXENE	42	0	0	42	0	0	74.67	93.34
HCL	0	0	0	0	0	0	0	0
MGCL2	0	0	0	0	0	0	0	0
SIO2	0	0	0	0	0	0	93.33	116.66
WATER	0	305.56	1589.38	0	305.56	1589.38	0	1918.27
NAOH	0	0	0	0	0	0	0	0
NACL	0	0	0	0	0	0	0	0
CO2	0	0	0	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0
MG++	0	0	0	0	0	0	0	23.33
H+	0	11	35.74	0	11	35.74	0	0.072
NA+	0	0	0	0	0	0	0	0
HCO3-	0	0	0	0	0	0	0	0
OH-	0	7.22E-14	5.22E-13	0	9.65E-13	9.93E-12	0	3.39E-09
CL-	0	11	35.74	0	11	35.74	0	46.74
CO3--	0	0	0	0	0	0	0	0
Total Flow kmol/hr	42	327.56	1660.86	42	327.56	1660.86	168	2198.42
Total Flow kg/hr	4216.33	5905.74	29936.23	4216.33	5905.74	29936.23	13103.69	53161.98
Total Flow cum/hr	1.26	5.92	29.98	1.26	6.04	30.61	4.36	41.19
Temperature C	25	25	20	70	70	70	70	70
Pressure atm	1	1	1	1	1	1	1	1
Vapor Frac	0	0	0	0	0	0	0	0
Liquid Frac	0	1	1	0	1	1	0	0.904
Solid Frac	1	0	0	1	0	0	1	0.096
Enthalpy kJ/kmol	-1548900	-272500	-277690	-1545100	-269440	-274180	-1191500	-369050
Enthalpy kJ/kg	-15429.2	-15113.86	-15406.39	-15390.95	-14944.1	-15211.3	-15275.8	-15261.5
Enthalpy kW	-18070.7	-24794.02	-128110	-18025.9	-24515.5	-126490	-55602.6	-225370
Entropy J/kmol-K	-291450	-156090	-159630	-279470	-146530	-148550	-221940	-157130
Entropy J/kg-K	-2903.2	-8657.548	-8856.015	-2783.832	-8127.22	-8241.52	-2845.42	-6497.67
Density kmol/cum	33.33	55.30	55.41	33.33	54.22	54.26	38.55	53.37
Density kg/cum	3346.29	997.01	998.67	3346.29	977.54	978.03	3007.11	1290.71
Average MW	100.39	18.03	18.02	100.39	18.03	18.02	78.00	24.18
Liq Vol 60F								

Table C-14: pH adjustment unit energy balance for 20% extraction and 65% carbonation

	LEACH-1	NAOH	LEACH-2
Substream: MIXED			
Mole Flow kmol/hr			
PYROXENE	0	0	0
HCL	0	0	0
MGCL2	0	0	0
SIO2	0	0	0
WATER	1918.27	3.704	1922.05
NAOH	0	0	0
NACL	0	0	0
CO2	0	0	0
MGCO3	0	0	0
MG++	23.33	0	23.33
H+	0.074	2.91E-18	1.27E-11
NA+	0	1	1
HCO3-	0	0	0
OH-	3.30E-09	1	0.926
CL-	46.73	0	46.73
CO3--	0	0	0
Total Flow kmol/hr	1988.41	5.704	1994.04
Total Flow kg/hr	36782.13	106.7257	36888.85
Total Flow cum/hr	35.74	0.0761	35.07
Temperature C	70	25	20
Pressure atm	1	1	1
Vapor Frac	0	0	0
Liquid Frac	1	1	1
Solid Frac	0	0	0
Enthalpy kJ/kmol	-282190	-266600	-285650
Enthalpy kJ/kg	-15255.17	-14248.65	-15441.11
Enthalpy kW	-155870	-422.416	-158220
Entropy J/kmol-K	-150280	-136210	-161180
Entropy J/kg-K	-8124.094	-7279.591	-8712.732
Density kmol/cum	55.63	74.92	56.86
Density kg/cum	1029.12	1401.79	1051.98
Average MW	18.50	18.71	18.50
Liq Vol 60F			

Table C-15: Mineral carbonation unit energy balance for 20% extraction and 65% carbonation

	LEACH-2	CO2	SOL-REC	SLURRY-2
Substream: MIXED				
Mole Flow kmol/hr				
PYROXENE	0	0	0	0
HCL	0	0	0	0
MGCL2	0	0	0	0
SIO2	0	0	0	0
WATER	1922.05	0	176.78	2087.10
NAOH	0	0	0	0
NACL	0	0	0	0
CO2	0	22.72	4.55	14.62
H2CO3	0	0	0	0
MGCO3	0	0	0	17.73
MG++	23.33	0	13.09	18.69
H+	3.99E-11	0	9.41E-09	29.27
NA+	0.9997	0	5.67	6.67
HCO3-	0	0	4.90	4.43E-07
OH-	0.9257	0	1.24E-06	1.40E-12
CL-	46.734	0	26.60	73.34
CO3--	0	0	0.177	4.46E-16
Total Flow kmol/hr	1994.04	22.72	231.76	2247.42
Total Flow kg/hr	36888.88	1000	5085.77	42974.64
Total Flow cum/hr	35.11	6.68	97.95	40.50
Temperature C	25	35	20	20
Pressure atm	1	57.48	1	1
Vapor Frac	0	1	0.017	0
Liquid Frac	1	0	0.983	0.992
Solid Frac	0	0	0	0.008
Enthalpy kJ/kmol	-285270	-396040	-291130	-287400
Enthalpy kJ/kg	-15420.45	-8998.79	-13266.96	-15029.73
Enthalpy kW	-158010	-2499.67	-18742.4	-179420
Entropy J/kmol-K	-160150	-35676.65	-144930	-158520
Entropy J/kg-K	-8657.06	-810.65	-6604.54	-8290.18
Density kmol/cum	56.80	3.40	2.37	55.50
Density kg/cum	1050.75	149.71	51.92	1061.20
Average MW	18.50	44.01	21.94	19.12
Liq Vol 60F		1.22		

C.5. Direct Aqueous Carbonation Process

Table C-16: Direct aqueous carbonation for 5% carbonation

	H2O	CO2	H2O-	CO2-	H2O-CO2	PYROX	PYROX-FD	PYR-REC	SOL-REC	SLURRY	SOLN	SPNT-SOL	SOLIDS	SIO2-PYR	MGCO3	PYR-SIO2
Substream: MIXED																
Mole Flow kmol/hr																
PYROX	0	0	0	0	0	86	86	360.8	0	424.4	0	0	424.4	424.4	0	63.7
WATER	998.3	0	998.3	0	975.5	0	0	0	18958	19955.8	19955.8	997.8	0	0	0	0
CO2	0	22.7	0	22.7	0	0	0	0	0	0	0	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	22.3	0	0	22.3	0	22.3	0
SIO2	0	0	0	0	0	0	0	126.6	0	148.9	0	0	148.9	148.9	0	22.3
H2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NAHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NACL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H+	0	0	0	0	22.7	0	0	0	7.3	7.7	7.7	0.4	0	0	0	0
NA+	29.5	0	29.5	0	29.5	0	0	0	559.9	589.3	589.3	29.5	0	0	0	0
OH-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CL-	18.0	0	18.0	0	18.0	0	0	0	341.4	359.3	359.3	18.0	0	0	0	0
HCO3-	11.5	0	11.5	0	34.2	0	0	0	225.8	237.7	237.7	11.9	0	0	0	0
Total Flow kmol/hr	1057.2	22.7	1057.2	22.7	1079.9	86	86	487.3	20092.4	21745.5	21149.8	1057.5	595.7	573.3	22.3	86
Total Flow kg/hr	20000.2	1000	20000.2	1000	21000.2	8633.4	8633.4	43821.0	380292	453745	400308	20015.4	53437.5	51554.2	1883.4	7733.1
Total Flow cum/hr	18.7	1.6	20.9	2.1	21.4	2.6	2.6	13.7	397.7	435.4	418.7	20.9	16.7	16.1	0.6	2.4
Temperature C	25	30	185	185	185	25	185	185	185	185	185	185	185	185	185	185
Pressure atm	1	150	150	150	150	1	1	150	150	150	150	150	150	150	150	150
Enthalpy kJ/kmol	-287130	-396840	-275350	-387300	-278130	-1548900	-1534300	-1370200	-275400	-305100	-275400	-275400	-1360000	-1370200	-1099300	-1370200
Enthalpy kJ/kg	-15177.6	-9017.08	-14554.6	-8800.4	-14302.8	-15429.2	-15283.2	-15237.5	-14550.2	-14622	-14550.2	-14550.2	-15160	-15237.5	-13038	-15237.5
Enthalpy kW	-84320.7	-2504.74	-80859.9	-2444.56	-83433.7	-37001.9	-36651.78	-185480	-1537000	-1843000	-1617900	-80896.8	-225030	-218210	-6820.97	-32731.5
Entropy J/kmol-K	-157360	-42628	-126500	-34709.1	-127650	-291450	-252350	-228510	-126510	-129320	-126510	-126510	-229080	-228510	-243800	-228510
Entropy J/kg-K	-8317.86	-968.602	-6686.79	-788.667	-6564.19	-2903.2	-2513.741	-2541.25	-6684.07	-6197.47	-6684.07	-6684.07	-2553.6	-2541.25	-2891.59	-2541.25

Table C-17: Direct aqueous carbonation for 20% carbonation

	H2O	CO2	H2O-	CO2-	H2O-CO2	PYROX	PYROX-FD	PYR-REC	SOL-REC	SLURRY	SOLN	SPNT-SOL	SOLIDS	SIO2-PYR	MGCO3	PYR-SIO2
Substream: MIXED																
Mole Flow kmol/hr																
PYROX	0	0	0	0	0	30	30	77.1	0	85.7	0	0	85.7	85.7	0	8.6
WATER	434.0	0	434.0	0	411.3	0	0	0	8221.2	8653.9	8653.9	432.7	0	0	0	0
CO2	0	22.7	0	22.7	0	0	0	0	0	0	0	0	0	0	0	0
MGCO3	0	0	0	0	0	0	0	0	0	21.4	0	0	21.4	0	21.4	0
SIO2	0	0	0	0	0	0	0	192.9	0	214.3	0	0	214.3	214.3	0	21.4
H2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NAHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NACL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H+	0	0	0	0	22.7	0	0	0	24.6	25.9	25.9	1.3	0	0	0	0
NA+	13	0	13	0	13	0	0	0	247.0	260.0	260.0	13.0	0	0	0	0
OH-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CL-	8	0	8	0	8	0	0	0	152.0	160.0	160.0	8.0	0	0	0	0
HCO3-	5	0	5	0	27.7	0	0	0	119.6	125.9	125.9	6.3	0	0	0	0
Total Flow kmol/hr	460.0	22.7	460.0	22.7	482.8	30	30	270	8764.3	9547.0	9225.6	461.3	321.4	300.0	21.4	30
Total Flow kg/hr	8706.7	1000	8706.7	1000	9706.7	3011.7	3011.7	19332.0	166494	198544	175257	8762.9	23286.7	21480	1806.7	2148
Total Flow cum/hr	8.1	1.6	9.1	2.1	9.5	0.9	0.9	6.7	173.5	190.7	182.6	9.1	8.0	7.4	0.6	0.7
Temperature C	25	30	185	185	185	25	185	184.9793	184.9793	185	184.9793	184.9793	184.9793	184.9793	184.9793	184.9793
Pressure atm	1	150	150	150	150	1	1	150	150	150	150	150	150	150	150	150
Enthalpy kJ/kmol	-287060	-396840	-275290	-387300	-281500	-1548900	-1534300	-1083000	-275660	-302880	-275660	-275660	-1084100	-1083000	-1099300	-1083000
Enthalpy kJ/kg	-15167.25	-9017.08	-14545.08	-8800.4	-13999.98	-15429.2	-15283.2	-15125.32	-14510.92	-14563.91	-14510.92	-14510.92	-14963.37	-15125.32	-13037.98	-15125.32
Enthalpy kW	-36682.45	-2504.74	-35177.7	-2444.56	-37748.24	-12907.64	-12785.5	-81222.79	-671110	-803220	-706430	-35321.46	-96790.93	-90247.55	-6543.376	-9024.755
Entropy J/kmol-K	-157250	-42628	-126420	-34709.1	-129440	-291450	-252350	-186780	-126520	-128670	-126520	-126520	-190580	-186780	-243800	-186780
Entropy J/kg-K	-8308.46	-968.602	-6679.405	-788.667	-6437.454	-2903.204	-2513.741	-2608.645	-6659.973	-6187.216	-6659.973	-6659.973	-2630.597	-2608.645	-2891.59	-2608.645

SimaPro Process Inputs Inventory Analysis

This section presents the outputs of carbon dioxide accounting conducted in SimaPro modelling software. This includes results for background and foreground processes for all the selected processes discussed in the Results and Discussions section of the dissertation. The data presented includes quantities of process input, the modelling method used (ReCiPe Midpoint), the impact category selected (Climate Change), and the processes that are used for the generation of the input.

D.1. Ammonium Salts Process

a. Ammonium Bisulphate Production

Table D-1: SimaPro results of carbon dioxide burdens of ammonium bisulphate production at 30% extraction

Calculation:	Analyze						
Results:	Inventory						
Product:	1035.99 kg Ammonium Bisulph (of project Ammon_Salts Background)						
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H						
Indicator:	Characterization						
Unit:	kg CO2 eq						
Skip unused:	No						
Category:	Climate change						
Cut-off:	0.13%						
Exclude infrastructure processes:	No						
Exclude long-term emissions:	No						
Sorted on item:	Substance						
Sort order:	Ascending						
No	Substance	Compartment	Unit	Total	Ammonium Bisulph	Ammonia, steam reforming, liquid, at plant/RER S	Sulphuric acid, liquid, at plant/RER S
	Total		kg CO2 eq	695.17	x	585.97	109.20
	Remaining substances		kg CO2 eq	1.64	x	0.548	1.10
1	Carbon dioxide, fossil	Air	kg CO2 eq	655.54	x	551.08	104.46
2	Dinitrogen monoxide	Air	kg CO2 eq	2.66	x	2.05	0.605
3	Methane, fossil	Air	kg CO2 eq	35.32	x	32.29	3.04

Table D-2: SimaPro results of carbon dioxide burdens of ammonium bisulphate production at 50% extraction

Calculation:	Analyze						
Results:	Inventory						
Product:	1035.99 kg Ammonium Bisulph (of project Ammon_Salts Background)						
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H						
Indicator:	Characterization						
Unit:	kg CO2 eq						
Skip unused:	No						
Category:	Climate change						
Cut-off:	0.13%						
Exclude infrastructure processes:	No						
Exclude long-term emissions:	No						
Sorted on item:	Substance						
Sort order:	Ascending						
No	Substance	Compartment	Unit	Total	Ammonium Bisulph	Ammonia, steam reforming, liquid, at plant/RER S	Sulphuric acid, liquid, at plant/RER S
	Total		kg CO2 eq	695.17	x	585.97	109.20
	Remaining substances		kg CO2 eq	1.64	x	0.548	1.10
1	Carbon dioxide, fossil	Air	kg CO2 eq	655.54	x	551.08	104.46
2	Dinitrogen monoxide	Air	kg CO2 eq	2.66	x	2.05	0.605
3	Methane, fossil	Air	kg CO2 eq	35.32	x	32.29	3.04

Table D-3: SimaPro results of carbon dioxide burdens of ammonium bisulphate production at 90% extraction

Calculation:	Analyze						
Results:	Inventory						
Product:	1151.1 kg Ammonium Bisulph (of project Ammon_Salts Background)						
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H						
Indicator:	Characterization						
Unit:	kg CO2 eq						
Skip unused:	No						
Category:	Climate change						
Cut-off:	0.13%						
Exclude infrastructure processes:	No						
Exclude long-term emissions:	No						
Sorted on item:	Substance						
Sort order:	Ascending						
No	Substance	Compartment	Unit	Total	Ammonium Bisulph	Ammonia, steam reforming, liquid, at plant/RER S	Sulphuric acid, liquid, at plant/RER S
	Total		kg CO2 eq	772.41	x	651.08	121.33
	Remaining substances		kg CO2 eq	1.83	x	0.609	1.22
1	Carbon dioxide, fossil	Air	kg CO2 eq	728.38	x	612.31	116.07
2	Dinitrogen monoxide	Air	kg CO2 eq	2.95	x	2.28	0.672
3	Methane, fossil	Air	kg CO2 eq	39.25	x	35.88	3.37

b. Ammonium Hydroxide Production

Table D-4: SimaPro results of carbon dioxide burdens of ammonium hydroxide production at 30% extraction

Calculation:	Analyze						
Results:	Inventory						
Product:	525.6876 kg Ammonium Hydroxide (of project Ammon_Salts Background)						
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H						
Indicator:	Characterization						
Unit:	kg CO2 eq						
Skip unused:	No						
Category:	Climate change						
Cut-off:	0.13%						
Exclude infrastructure processes:	No						
Exclude long-term emissions:	No						
Sorted on item:	Substance						
Sort order:	Ascending						
No	Substance	Compartment	Unit	Total	Ammonium Hydroxide	Ammonia, steam reforming, liquid, at plant/ RER S	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	489.96	x	488.19	1.76
	Remaining substances		kg CO2 eq	0.525	x	0.453	0.071
1	Carbon dioxide, fossil	Air	kg CO2 eq	459.12	x	459.12	x
2	Carbon dioxide, land transformation	Air	kg CO2 eq	1.68	x	0.003	1.67
3	Dinitrogen monoxide	Air	kg CO2 eq	1.73	x	1.71	0.016
4	Methane, fossil	Air	kg CO2 eq	26.90	x	26.90	x

Table D-5: SimaPro results of carbon dioxide burdens of ammonium hydroxide production at 50% extraction

Calculation:	Analyze						
Results:	Inventory						
Product:	280.3667 kg Ammonium Hydroxide (of project Ammon_Salts Background)						
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H						
Indicator:	Characterization						
Unit:	kg CO2 eq						
Skip unused:	No						
Category:	Climate change						
Cut-off:	0.13%						
Exclude infrastructure processes:	No						
Exclude long-term emissions:	No						
Sorted on item:	Substance						
Sort order:	Ascending						
No	Substance	Compartment	Unit	Total	Ammonium Hydroxide	Ammonia, steam reforming, liquid, at plant/ RER S	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	261.31	x	260.37	0.939
	Remaining substances		kg CO2 eq	0.280	x	0.242	0.038
1	Carbon dioxide, fossil	Air	kg CO2 eq	244.87	x	244.87	x
2	Carbon dioxide, land transformation	Air	kg CO2 eq	0.895	x	0.002	0.893
3	Dinitrogen monoxide	Air	kg CO2 eq	0.921	x	0.912	0.009
4	Methane, fossil	Air	kg CO2 eq	14.35	x	14.35	x

Table D-6: SimaPro results of carbon dioxide burdens of ammonium hydroxide production at 90% extraction

Calculation:	Analyze						
Results:	Inventory						
Product:	210.275 kg Ammonium Hydroxide (of project Ammon_Salts Background)						
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H						
Indicator:	Characterization						
Unit:	kg CO2 eq						
Skip unused:	No						
Category:	Climate change						
Cut-off:	0.13%						
Exclude infrastructure processes:	No						
Exclude long-term emissions:	No						
Sorted on item:	Substance						
Sort order:	Ascending						
No	Substance	Compartment	Unit	Total	Ammonium Hydroxide	Ammonia, steam reforming, liquid, at plant/RER S	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	195.98	x	195.28	0.705
	Remaining substances		kg CO2 eq	0.210	x	0.181	0.028
1	Carbon dioxide, fossil	Air	kg CO2 eq	183.65	x	183.65	x
2	Carbon dioxide, land transformation	Air	kg CO2 eq	0.671	x	0.001	0.670
3	Dinitrogen monoxide	Air	kg CO2 eq	0.691	x	0.684	0.006
4	Methane, fossil	Air	kg CO2 eq	10.76	x	10.76	x

c. Heat Requirements

Table D-7: SimaPro results of carbon dioxide burdens of process heat requirements at 30% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	104486.21 MJ Heat Requirements (of project Ammon_Salts Background)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Heat Requirements	Heat, natural gas, at industrial furnace >100kW/RER S
	Total		kg CO2 eq	7479.22	x	7479.22
	Remaining substances		kg CO2 eq	9.55	x	9.55
1	Carbon dioxide, fossil	Air	kg CO2 eq	7028.67	x	7028.67
2	Methane, fossil	Air	kg CO2 eq	441.00	x	441.00

Table D-8: SimaPro results of carbon dioxide burdens of process heat requirements at 50% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	77649.16 MJ Heat Requirements (of project Ammon_Salts Background)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Heat Requirements	Heat, natural gas, at industrial furnace >100kW/RER S
	Total		kg CO2 eq	5558.20	x	5558.20
	Remaining substances		kg CO2 eq	7.09	x	7.09
1	Carbon dioxide, fossil	Air	kg CO2 eq	5223.37	x	5223.37
2	Methane, fossil	Air	kg CO2 eq	327.73	x	327.73

Table D-9: SimaPro results of carbon dioxide burdens of process heat requirements at 90% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	75323.53 MJ Heat Requirements (of project Ammon_Salts Background)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Heat Requirements	Heat, natural gas, at industrial furnace >100kW/RER S
	Total		kg CO2 eq	5391.73	x	5391.73
	Remaining substances		kg CO2 eq	6.88	x	6.88
1	Carbon dioxide, fossil	Air	kg CO2 eq	5066.93	x	5066.93
2	Methane, fossil	Air	kg CO2 eq	317.92	x	317.92

d. Electricity Requirements

Table D-10: SimaPro results of carbon dioxide burdens of compression electricity requirements (All extraction efficiencies)

Calculation:	Analyze					
Results:	Inventory					
Product:	214.7193047 MJ Compression Electricity (of project Ammon_Salts Background)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Compression Electricity	South African medium voltage electricity production (at grid), plus imports System
	Total		kg CO2 eq	60.49	x	60.49
	Remaining substances		kg CO2 eq	0.033	x	0.033
1	Carbon dioxide, fossil	Air	kg CO2 eq	57.29	x	57.29
2	Dinitrogen monoxide	Air	kg CO2 eq	0.350	x	0.350
3	Methane, fossil	Air	kg CO2 eq	2.72	x	2.72
4	Sulfur hexafluoride	Air	kg CO2 eq	0.102	x	0.102

e. Process Water Requirements

Table D-11: SimaPro results of carbon dioxide burdens of process water requirements at 30% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	13940.396 kg Supply Water (of project Ammon_Salts Background)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Supply Water	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	90.81	x	90.81
	Remaining substances		kg CO2 eq	0.086	x	0.086
1	Carbon dioxide, land transformation	Air	kg CO2 eq	86.32	x	86.32
2	Dinitrogen monoxide	Air	kg CO2 eq	0.830	x	0.830
3	Methane	Air	kg CO2 eq	3.58	x	3.58

Table D-12: SimaPro results of carbon dioxide burdens of process water requirements at 50% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	10437.425 kg Supply Water (of project Ammon_Salts Background)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Supply Water	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	67.99	x	67.99
	Remaining substances		kg CO2 eq	0.064	x	0.064
1	Carbon dioxide, land transformation	Air	kg CO2 eq	64.63	x	64.63
2	Dinitrogen monoxide	Air	kg CO2 eq	0.621	x	0.621
3	Methane	Air	kg CO2 eq	2.68	x	2.68

Table D-13: SimaPro results of carbon dioxide burdens of process water requirements at 90% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	10151.468 kg Supply Water (of project Ammon_Salts Background)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Supply Water	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	66.13	x	66.13
	Remaining substances		kg CO2 eq	0.062	x	0.062
1	Carbon dioxide, land transformation	Air	kg CO2 eq	62.86	x	62.86
2	Dinitrogen monoxide	Air	kg CO2 eq	0.604	x	0.604
3	Methane	Air	kg CO2 eq	2.61	x	2.61

D.2. Lackner's HCl Multistage Process

a. Hydrochloric Acid Production

Table D-14: SimaPro results of carbon dioxide burdens of hydrochloric acid production at 30% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	1826.678 kg Process Hydrochloric Acid (of project Lackner Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Hydrochloric Acid	Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant/RER S
	Total		kg CO2 eq	2394.18	x	2394.1755
	Remaining substances		kg CO2 eq	3.70818	x	3.7081831
1	Carbon dioxide, fossil	Air	kg CO2 eq	2239.56	x	2239.5616
2	Dinitrogen monoxide	Air	kg CO2 eq	20.2988	x	20.298817
3	Methane, fossil	Air	kg CO2 eq	115.061	x	115.06064
4	Methane, tetrachloro-, CFC-10	Air	kg CO2 eq	5.64433	x	5.6443254
5	Methane, tetrafluoro-, CFC-14	Air	kg CO2 eq	3.47827	x	3.4782704
6	Sulfur hexafluoride	Air	kg CO2 eq	6.42373	x	6.4237328

Table D-15: SimaPro results of carbon dioxide burdens of hydrochloric acid production at 50% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	2227.745 kg Process Hydrochloric Acid (of project Lackner Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Hydrochloric Acid	Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant/RER S
	Total		kg CO2 eq	2919.84	x	2919.8428
	Remaining substances		kg CO2 eq	4.52236	x	4.522355
1	Carbon dioxide, fossil	Air	kg CO2 eq	2731.28	x	2731.2817
2	Dinitrogen monoxide	Air	kg CO2 eq	24.7556	x	24.755643
3	Methane, fossil	Air	kg CO2 eq	140.323	x	140.32345
4	Methane, tetrachloro-, CFC-10	Air	kg CO2 eq	6.8836	x	6.8835984
5	Methane, tetrafluoro-, CFC-14	Air	kg CO2 eq	4.24196	x	4.2419624
6	Sulfur hexafluoride	Air	kg CO2 eq	7.83413	x	7.8341332

Table D-16: SimaPro results of carbon dioxide burdens of hydrochloric acid production at 90% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	2049.088 kg Process Hydrochloric Acid (of project Lackner Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Hydrochloric Acid	Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant/RER S
	Total		kg CO2 eq	2685.68	x	2685.6821
	Remaining substances		kg CO2 eq	4.15968	x	4.1596786
1	Carbon dioxide, fossil	Air	kg CO2 eq	2512.24	x	2512.2429
2	Dinitrogen monoxide	Air	kg CO2 eq	22.7703	x	22.770331
3	Methane, fossil	Air	kg CO2 eq	129.07	x	129.07003
4	Methane, tetrachloro-, CFC-10	Air	kg CO2 eq	6.33156	x	6.331559
5	Methane, tetrafluoro-, CFC-14	Air	kg CO2 eq	3.90177	x	3.9017726
6	Sulfur hexafluoride	Air	kg CO2 eq	7.20586	x	7.2058643

b. Heat Requirements

Table D-17: SimaPro results of carbon dioxide burdens of process heat requirements at 30% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	229961.53 MJ Heat Requirements (of project Lackner Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Heat Requirements	Natural gas, burned in industrial furnace >100kW/RER S
	Total		kg CO2 eq	15677.003	x	15677.003
	Remaining substances		kg CO2 eq	20.011174	x	20.011174
1	Carbon dioxide, fossil	Air	kg CO2 eq	14732.575	x	14732.575
2	Methane, fossil	Air	kg CO2 eq	924.41665	x	924.41665

Table D-18: SimaPro results of carbon dioxide burdens of process heat requirements at 50% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	257971.86 MJ Heat Requirements (of project Lackner Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Heat Requirements	Natural gas, burned in industrial furnace >100kW/RER S
	Total		kg CO2 eq	17586.531	x	17586.531
	Remaining substances		kg CO2 eq	22.448623	x	22.448623
1	Carbon dioxide, fossil	Air	kg CO2 eq	16527.068	x	16527.068
2	Methane, fossil	Air	kg CO2 eq	1037.0147	x	1037.0147

Table D-19: SimaPro results of carbon dioxide burdens of process heat requirements at 90% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	280513.12 MJ Heat Requirements (of project Lackner Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Heat Requirements	Natural gas, burned in industrial furnace >100kW/RER S
	Total		kg CO2 eq	19123.22	x	19123.22
	Remaining substances		kg CO2 eq	24.410156	x	24.410156
1	Carbon dioxide, fossil	Air	kg CO2 eq	17971.182	x	17971.182
2	Methane, fossil	Air	kg CO2 eq	1127.6277	x	1127.6277

c. Process Water Requirements

Table D-20: SimaPro results of carbon dioxide burdens of process water requirements at 30% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	25071.27 kg Process Water Supply (of project Lackner Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Water Supply	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	163.326	x	163.326
	Remaining substances		kg CO2 eq	0.154061	x	0.15406133
1	Carbon dioxide, land transformation	Air	kg CO2 eq	155.2377	x	155.23771
2	Dinitrogen monoxide	Air	kg CO2 eq	1.492579	x	1.4925785
3	Methane	Air	kg CO2 eq	6.441655	x	6.4416553

Table D-21: SimaPro results of carbon dioxide burdens of process water requirements at 50% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	28123.85 kg Process Water Supply (of project Lackner Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Water Supply	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	183.2119	x	183.21194
	Remaining substances		kg CO2 eq	0.172819	x	0.17281923
1	Carbon dioxide, land transformation	Air	kg CO2 eq	174.1389	x	174.13885
2	Dinitrogen monoxide	Air	kg CO2 eq	1.674309	x	1.674309
3	Methane	Air	kg CO2 eq	7.225966	x	7.2259661

Table D-22: SimaPro results of carbon dioxide burdens of process water requirements at 90% extraction

Calculation:	Analyze					
Results:	Inventory					
Product:	30575.93 kg Process Water Supply (of project Lackner Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Water Supply	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	199.1859	x	199.18594
	Remaining substances		kg CO2 eq	0.187887	x	0.18788711
1	Carbon dioxide, land transformation	Air	kg CO2 eq	189.3218	x	189.32178
2	Dinitrogen monoxide	Air	kg CO2 eq	1.82029	x	1.8202897
3	Methane	Air	kg CO2 eq	7.855988	x	7.8559882

D.3. Åbo Akademi University (AAU) Process

a. Ammonium Sulphate Production

Table D-23: SimaPro results of carbon dioxide burdens of ammonium bisulphate production (All extraction efficiencies)

Calculation:	Analyze						
Results:	Inventory						
Product:	396.4218 kg Ammonium Sulphate Supply (of project AAU Process)						
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H						
Indicator:	Characterization						
Unit:	kg CO2 eq						
Skip unused:	No						
Category:	Climate change						
Cut-off:	0.13%						
Exclude infrastructure processes:	No						
Exclude long-term emissions:	No						
Sorted on item:	Substance						
Sort order:	Ascending						
No	Substance	Compartment	Unit	Total	Ammonium Sulphate Supply	Ammonia, steam reforming, liquid, at plant/RER S	Sulphuric acid, liquid, at plant/RER S
	Total		kg CO2 eq	231.6711	x	195.26976	36.401304
	Remaining substances		kg CO2 eq	0.547846	x	0.18263366	0.36521277
1	Carbon dioxide, fossil	Air	kg CO2 eq	218.4652	x	183.64243	34.822736
2	Dinitrogen monoxide	Air	kg CO2 eq	0.885976	x	0.68432877	0.20164763
3	Methane, fossil	Air	kg CO2 eq	11.77208	x	10.760368	1.0117078

b. Heat Requirements

Table D-24: SimaPro results of carbon dioxide burdens of process heat requirements at 66% extraction and 55% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	14236.82663 MJ Plant Supply Energy (of project AAU Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Plant Supply Energy	Heat, natural gas, at industrial furnace >100kW/RER S
	Total		kg CO2 eq	1019.086	x	1019.0856
	Remaining substances		kg CO2 eq	1.300829	x	1.3008293
1	Carbon dioxide, fossil	Air	kg CO2 eq	957.6957	x	957.69567
2	Methane, fossil	Air	kg CO2 eq	60.08913	x	60.089126

Table D-25: SimaPro results of carbon dioxide burdens of process heat requirements at 100% extraction and 80% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	8853.981264 MJ Plant Supply Energy (of project AAU Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Plant Supply Energy	Heat, natural gas, at industrial furnace >100kW/RER S
	Total		kg CO2 eq	633.7764	x	633.77642
	Remaining substances		kg CO2 eq	0.808995	x	0.80899478
1	Carbon dioxide, fossil	Air	kg CO2 eq	595.5976	x	595.59758
2	Methane, fossil	Air	kg CO2 eq	37.36985	x	37.369845

c. Electricity Requirements

Table D-26: SimaPro results of carbon dioxide burdens of compression electricity requirements (All extraction efficiencies)

Calculation:	Analyze				
Results:	Inventory				
Product:	299.4457878 MJ South African medium voltage electricity production (at grid), plus imports System (of project AAU Process)				
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H				
Indicator:	Characterization				
Unit:	kg CO2 eq				
Skip unused:	No				
Category:	Climate change				
Cut-off:	0.13%				
Exclude infrastructure processes:	No				
Exclude long-term emissions:	No				
Sorted on item:	Substance				
Sort order:	Ascending				
No	Substance	Compartment	Unit	Total	South African medium voltage electricity production (at grid), plus imports System
	Total		kg CO2 eq	84.365214	84.365214
	Remaining substances		kg CO2 eq	0.045687686	0.045687686
1	Carbon dioxide, fossil	Air	kg CO2 eq	79.890709	79.890709
2	Dinitrogen monoxide	Air	kg CO2 eq	0.48753267	0.48753267
3	Methane, fossil	Air	kg CO2 eq	3.7986412	3.7986412
4	Sulfur hexafluoride	Air	kg CO2 eq	0.14264333	0.14264333

d. Process Water Requirements

Table D-27: SimaPro results of carbon dioxide burdens of process water requirements (All extraction efficiencies)

Calculation:	Analyze					
Results:	Inventory					
Product:	848.19 kg Process Water Supply (of project AAU Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Water Supply	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	5.525507	x	5.5255072
	Remaining substances		kg CO2 eq	0.005212	x	0.005212073
1	Carbon dioxide, land transformation	Air	kg CO2 eq	5.251871	x	5.2518709
2	Dinitrogen monoxide	Air	kg CO2 eq	0.050496	x	0.050495652
3	Methane	Air	kg CO2 eq	0.217929	x	0.21792863

D.4. Mineral Acid pH-Swing Process

a. Hydrochloric Acid Production

Table D-28: SimaPro results of carbon dioxide burdens of hydrochloric acid production at 20% extraction and 65% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	765.67 kg Process Hydrochloric Acid (of project Mineral Acid Process - pH Swing)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Hydrochloric Acid	Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant/RER S
	Total		kg CO2 eq	1003.5422	x	1003.5422
	Remaining substances		kg CO2 eq	1.5543213	x	1.5543213
1	Carbon dioxide, fossil	Air	kg CO2 eq	938.7342	x	938.7342
2	Dinitrogen monoxide	Air	kg CO2 eq	8.5084483	x	8.5084483
3	Methane, fossil	Air	kg CO2 eq	48.228796	x	48.228796
4	Methane, tetrachloro-, CFC-10	Air	kg CO2 eq	2.3658744	x	2.3658744
5	Methane, tetrafluoro-, CFC-14	Air	kg CO2 eq	1.4579511	x	1.4579511
6	Sulfur hexafluoride	Air	kg CO2 eq	2.6925706	x	2.6925706

Table D-29: SimaPro results of carbon dioxide burdens of hydrochloric acid production at 30% extraction and 90% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	1203.20 kg Process Hydrochloric Acid (of project Mineral Acid Process - pH Swing)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Hydrochloric Acid	Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant/RER S
	Total		kg CO2 eq	1577.0004	x	1577.0004
	Remaining substances		kg CO2 eq	2.4425136	x	2.4425136
1	Carbon dioxide, fossil	Air	kg CO2 eq	1475.159	x	1475.159
2	Dinitrogen monoxide	Air	kg CO2 eq	13.370466	x	13.370466
3	Methane, fossil	Air	kg CO2 eq	75.788377	x	75.788377
4	Methane, tetrachloro-, CFC-10	Air	kg CO2 eq	3.7178158	x	3.7178158
5	Methane, tetrafluoro-, CFC-14	Air	kg CO2 eq	2.2910742	x	2.2910742
6	Sulfur hexafluoride	Air	kg CO2 eq	4.2311975	x	4.2311975

Table D-30: SimaPro results of carbon dioxide burdens of hydrochloric acid production at 50% extraction and 90% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	1677.19 kg Process Hydrochloric Acid (of project Mineral Acid Process - pH Swing)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Hydrochloric Acid	Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant/RER S
	Total		kg CO2 eq	2198.2458	x	2198.2458
	Remaining substances		kg CO2 eq	3.4047203	x	3.4047203
1	Carbon dioxide, fossil	Air	kg CO2 eq	2056.2848	x	2056.2848
2	Dinitrogen monoxide	Air	kg CO2 eq	18.637643	x	18.637643
3	Methane, fossil	Air	kg CO2 eq	105.64454	x	105.64454
4	Methane, tetrachloro-, CFC-10	Air	kg CO2 eq	5.1824165	x	5.1824165
5	Methane, tetrafluoro-, CFC-14	Air	kg CO2 eq	3.1936227	x	3.1936227
6	Sulfur hexafluoride	Air	kg CO2 eq	5.8980403	x	5.8980403

b. Sodium Hydroxide Production

Table D-31: SimaPro results of carbon dioxide burdens of hydrochloric acid production (All Cases)

Calculation:	Analyze					
Results:	Inventory					
Product:	799.94 kg Process Sodium Hydroxide (of project Mineral Acid Process - pH Swing)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Sodium Hydroxide	Sodium hydroxide, 50% in H2O, production mix, at plant/RER S
	Total		kg CO2 eq	877.0619	x	877.06192
	Remaining substances		kg CO2 eq	2.253136	x	2.2531361
1	Carbon dioxide, fossil	Air	kg CO2 eq	829.1078	x	829.10776
2	Dinitrogen monoxide	Air	kg CO2 eq	7.670804	x	7.6708039
3	Methane, fossil	Air	kg CO2 eq	35.54612	x	35.54612
4	Sulfur hexafluoride	Air	kg CO2 eq	2.4841	x	2.4840997

c. Heat Requirements

Table D-32: SimaPro results of carbon dioxide burdens of process heat requirements at 20% extraction and 65% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	14760.47147 MJ Heat Supply (of project Mineral Acid Process - pH Swing)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Heat Supply	Natural gas, burned in industrial furnace low-NOx >100kW/RER S
	Total		kg CO2 eq	1033.097	x	1033.0973
	Remaining substances		kg CO2 eq	1.648837	x	1.6488372
1	Carbon dioxide, fossil	Air	kg CO2 eq	971.0144	x	971.01437
2	Methane, fossil	Air	kg CO2 eq	60.4341	x	60.434096

Table D-33: SimaPro results of carbon dioxide burdens of process heat requirements at 30% extraction and 90% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	22378.79925 MJ Heat Supply (of project Mineral Acid Process - pH Swing)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Heat Supply	Natural gas, burned in industrial furnace low-NOx >100kW/RER S
	Total		kg CO2 eq	1566.31	x	1566.3102
	Remaining substances		kg CO2 eq	2.499852	x	2.4998522
1	Carbon dioxide, fossil	Air	kg CO2 eq	1472.184	x	1472.1844
2	Methane, fossil	Air	kg CO2 eq	91.62597	x	91.62597

Table D-34: SimaPro results of carbon dioxide burdens of process heat requirements at 50% extraction and 90% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	30617.4825 MJ Heat Supply (of project Mineral Acid Process - pH Swing)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Heat Supply	Natural gas, burned in industrial furnace low-NOx >100kW/RER S
	Total		kg CO2 eq	2142.942	x	2142.9423
	Remaining substances		kg CO2 eq	3.420165	x	3.4201648
1	Carbon dioxide, fossil	Air	kg CO2 eq	2014.164	x	2014.1644
2	Methane, fossil	Air	kg CO2 eq	125.3578	x	125.35778

d. Process Water Requirements

Table D-35: SimaPro results of carbon dioxide burdens of process water requirements at 20% extraction and 65% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	11843.38 kg Supply Water (of project Mineral Acid Process - pH Swing)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Supply Water	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	77.15333	x	77.153329
	Remaining substances		kg CO2 eq	0.072777	x	0.072776802
1	Carbon dioxide, land transformation	Air	kg CO2 eq	73.33251	x	73.332511
2	Dinitrogen monoxide	Air	kg CO2 eq	0.705077	x	0.70507693
3	Methane	Air	kg CO2 eq	3.042964	x	3.042964

Table D-36: SimaPro results of carbon dioxide burdens of process water requirements at 30% extraction and 90% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	17848.48 kg Supply Water (of project Mineral Acid Process - pH Swing)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Supply Water	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	116.2734	x	116.27337
	Remaining substances		kg CO2 eq	0.109678	x	0.10967775
1	Carbon dioxide, land transformation	Air	kg CO2 eq	110.5152	x	110.51523
2	Dinitrogen monoxide	Air	kg CO2 eq	1.062581	x	1.0625811
3	Methane	Air	kg CO2 eq	4.585877	x	4.5858768

Table D-37: SimaPro results of carbon dioxide burdens of process water requirements at 50% extraction and 90% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	24353.99 kg Supply Water (of project Mineral Acid Process - pH Swing)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Supply Water	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	158.6533	x	158.65331
	Remaining substances		kg CO2 eq	0.149654	x	0.14965369
1	Carbon dioxide, land transformation	Air	kg CO2 eq	150.7964	x	150.79641
2	Dinitrogen monoxide	Air	kg CO2 eq	1.449876	x	1.4498763
3	Methane	Air	kg CO2 eq	6.257362	x	6.2573618

D.5. Direct Aqueous Carbonation Process

a. Sodium Chloride Production

Table D-38: SimaPro results of carbon dioxide burdens of sodium chloride requirements at 5% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	1050.09375 kg Supply of Process Sodium Chloride (of project Direct Carbonation)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartn	Unit	Total	Supply of Process Sodium Chloride	Sodium chloride, brine solution, at plant/RER S
	Total		kg CO2 eq	118.7343	x	118.73432
	Remaining substances		kg CO2 eq	0.097518	x	0.097518228
1	Carbon dioxide, fossil	Air	kg CO2 eq	111.8259	x	111.82587
2	Dinitrogen monoxide	Air	kg CO2 eq	0.949265	x	0.94926473
3	Ethane, hexafluoro-, HFC-116	Air	kg CO2 eq	0.167525	x	0.16752492
4	Methane, fossil	Air	kg CO2 eq	4.727168	x	4.7271675
5	Methane, tetrafluoro-, CFC-14	Air	kg CO2 eq	0.777435	x	0.77743454
6	Sulfur hexafluoride	Air	kg CO2 eq	0.189537	x	0.18953659

Table D-39: SimaPro results of carbon dioxide burdens of sodium chloride requirements at 20% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	467.52 kg Supply of Process Sodium Chloride (of project Direct Carbonation)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartn	Unit	Total	Supply of Process Sodium Chloride	Sodium chloride, brine solution, at plant/RER S
	Total		kg CO2 eq	52.86258	x	52.862583
	Remaining substances		kg CO2 eq	0.043417	x	0.043416811
1	Carbon dioxide, fossil	Air	kg CO2 eq	49.78682	x	49.786823
2	Dinitrogen monoxide	Air	kg CO2 eq	0.422629	x	0.42262917
3	Ethane, hexafluoro-, HFC-116	Air	kg CO2 eq	0.074585	x	0.074585008
4	Methane, fossil	Air	kg CO2 eq	2.104617	x	2.1046172
5	Methane, tetrafluoro-, CFC-14	Air	kg CO2 eq	0.346127	x	0.34612738
6	Sulfur hexafluoride	Air	kg CO2 eq	0.084385	x	0.084384986

b. Sodium Bicarbonate Production

Table D-40: SimaPro results of carbon dioxide burdens of sodium bicarbonate requirements at 5% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	966 kg Process Supply Sodium Bicarbonate (of project Direct Carbonation)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Supply Sodium Bicarbonate	Sodium carbonate from ammonium chloride production, at plant/GLO S
	Total		kg CO2 eq	1015.949	x	1015.9494
	Remaining substances		kg CO2 eq	2.013112	x	2.0131116
1	Carbon dioxide, fossil	Air	kg CO2 eq	910.4894	x	910.48943
2	Dinitrogen monoxide	Air	kg CO2 eq	5.353886	x	5.353886
3	Methane, fossil	Air	kg CO2 eq	96.57265	x	96.572646
4	Methane, tetrafluoro-, CFC-14	Air	kg CO2 eq	1.520369	x	1.5203687

Table D-41: SimaPro results of carbon dioxide burdens of sodium bicarbonate requirements at 20% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	420 kg Process Supply Sodium Bicarbonate (of project Direct Carbonation)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Supply Sodium Bicarbonate	Sodium carbonate from ammonium chloride production, at plant/GLO S
	Total		kg CO2 eq	441.7172	x	441.71715
	Remaining substances		kg CO2 eq	0.875266	x	0.8752659
1	Carbon dioxide, fossil	Air	kg CO2 eq	395.865	x	395.86497
2	Dinitrogen monoxide	Air	kg CO2 eq	2.327777	x	2.3277765
3	Methane, fossil	Air	kg CO2 eq	41.98811	x	41.988107
4	Methane, tetrafluoro-, CFC-14	Air	kg CO2 eq	0.66103	x	0.66102987

c. Heat Requirements

Table D-42: SimaPro results of carbon dioxide burdens of heat requirements at 5% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	13936.00997 MJ Process Heat Supply (of project Direct Carbonation)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Heat Supply	Heat, natural gas, at industrial furnace >100kW/RER S
	Total		kg CO2 eq	997.55288	x	997.55288
	Remaining substances		kg CO2 eq	1.2733435	x	1.2733435
1	Carbon dioxide, fossil	Air	kg CO2 eq	937.46006	x	937.46006
2	Methane, fossil	Air	kg CO2 eq	58.819475	x	58.819475

Table D-43: SimaPro results of carbon dioxide burdens of heat requirements at 20% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	6073.469636 MJ Process Heat Supply (of project Direct Carbonation)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.14%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Heat Supply	Heat, natural gas, at industrial furnace >100kW/RER S
	Total		kg CO2 eq	434.74475	x	434.74475
	Remaining substances		kg CO2 eq	0.55493739	x	0.55493739
1	Carbon dioxide, fossil	Air	kg CO2 eq	408.55562	x	408.55562
2	Methane, fossil	Air	kg CO2 eq	25.634188	x	25.634188

d. Process Water Requirements

Table D-44: SimaPro results of carbon dioxide burdens of process water requirements at 5% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	17984.00 kg Process Water Supply (of project AAU Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Water Supply	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	117.1562	x	117.15621
	Remaining substances		kg CO2 eq	0.110511	x	0.11051051
1	Carbon dioxide, land transformation	Air	kg CO2 eq	111.3544	x	111.35435
2	Dinitrogen monoxide	Air	kg CO2 eq	1.070649	x	1.070649
3	Methane	Air	kg CO2 eq	4.620697	x	4.6206965

Table D-45: SimaPro results of carbon dioxide burdens of process water requirements at 20% carbonation

Calculation:	Analyze					
Results:	Inventory					
Product:	7819.13 kg Process Water Supply (of project AAU Process)					
Method:	ReCiPe Midpoint (H) V1.06 / World ReCiPe H					
Indicator:	Characterization					
Unit:	kg CO2 eq					
Skip unused:	No					
Category:	Climate change					
Cut-off:	0.13%					
Exclude infrastructure processes:	No					
Exclude long-term emissions:	No					
Sorted on item:	Substance					
Sort order:	Ascending					
No	Substance	Compartment	Unit	Total	Process Water Supply	Process water, ion exchange, production mix, at plant, from surface water RER S
	Total		kg CO2 eq	50.93748	x	50.937478
	Remaining substances		kg CO2 eq	0.048048	x	0.048048046
1	Carbon dioxide, land transformation	Air	kg CO2 eq	48.41493	x	48.414932
2	Dinitrogen monoxide	Air	kg CO2 eq	0.4655	x	0.46549956
3	Methane	Air	kg CO2 eq	2.008998	x	2.0089984

Aspen Plus Simulation Diagrams

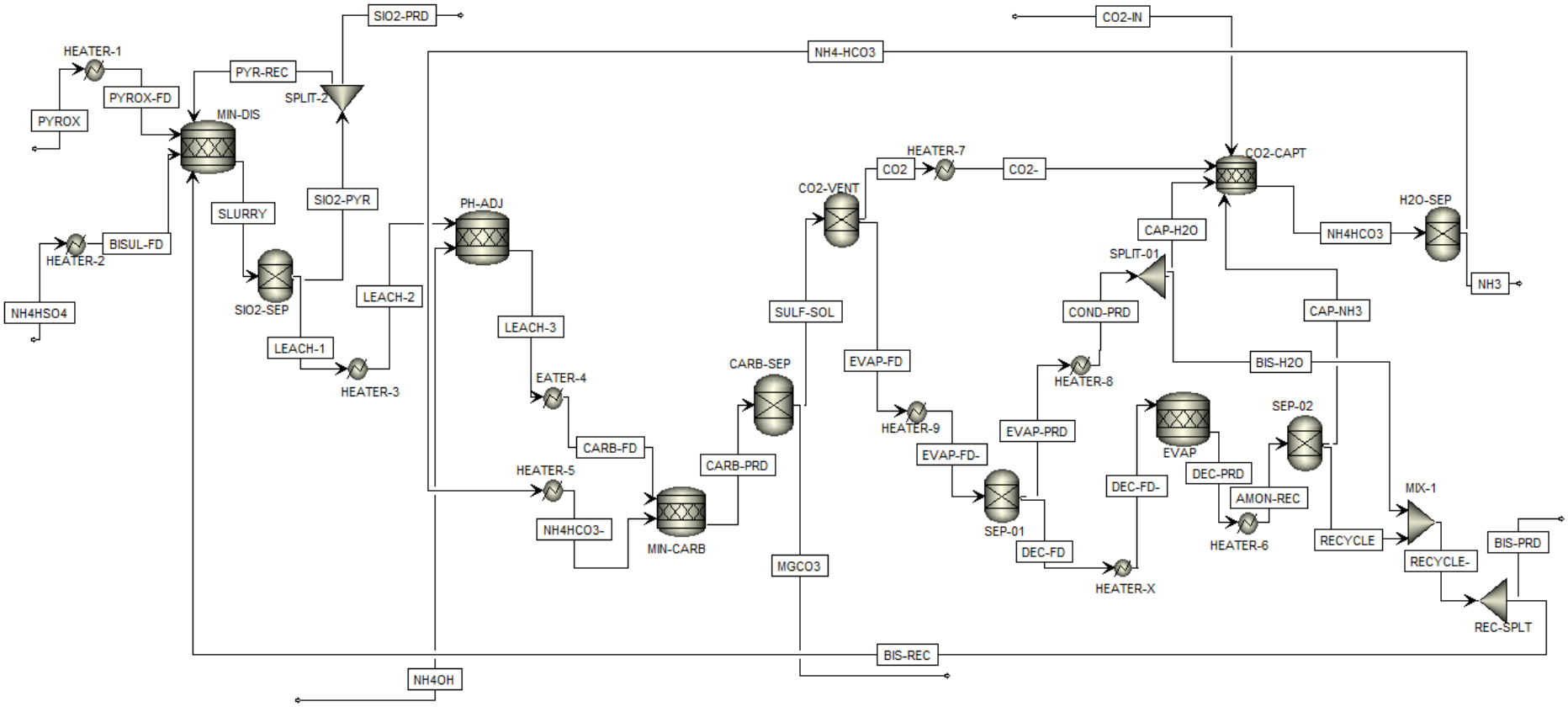

Figure E-1: Ammonium Salts process Aspen Plus simulation diagram

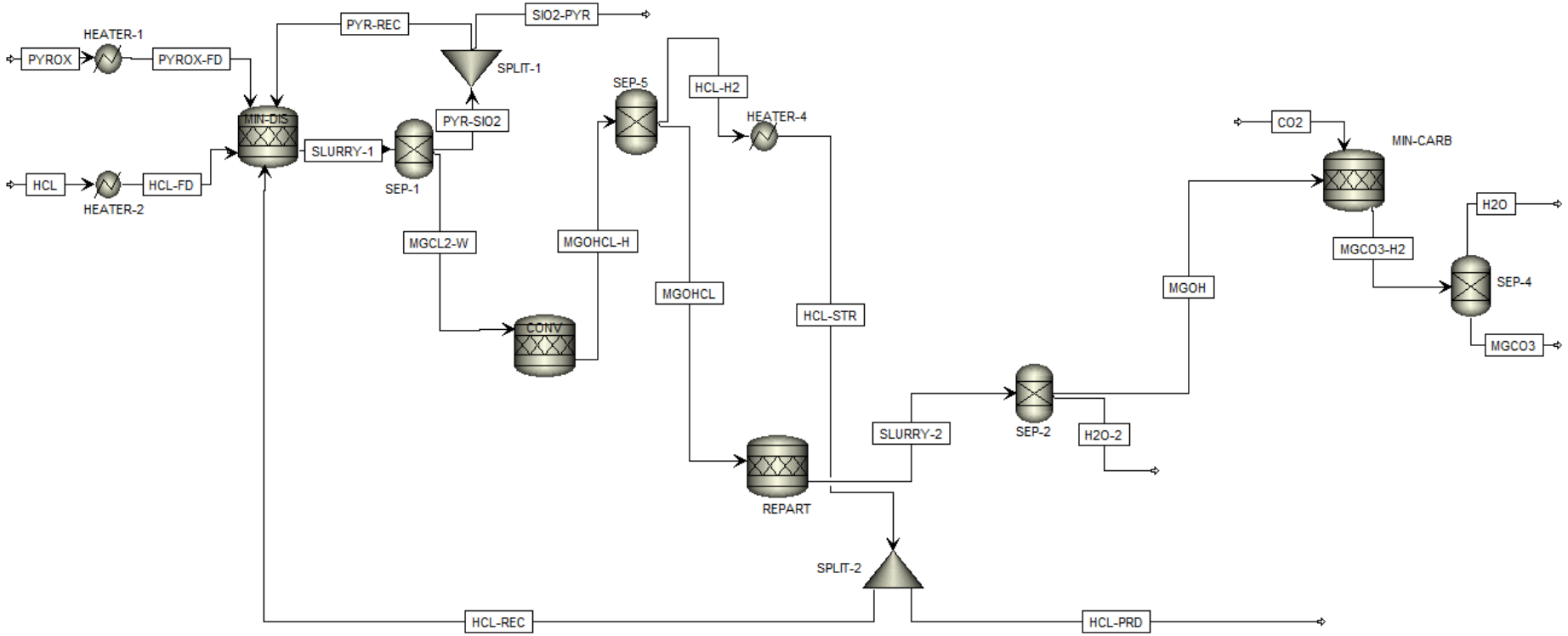

Figure E-2: Lackner's HCl process Aspen simulation diagram

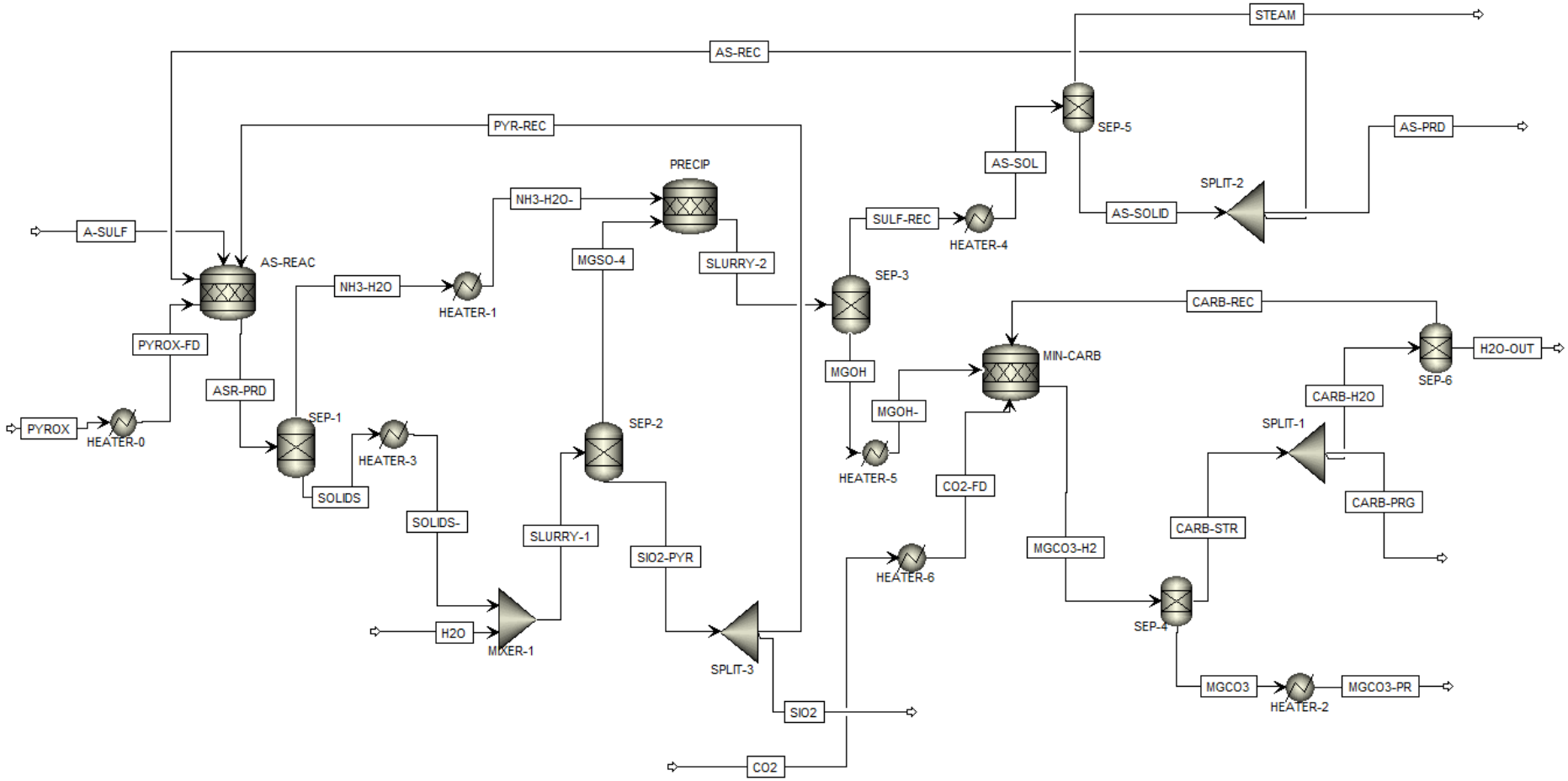

Figure E-3: Åbo Akademi University process Aspen Plus simulation diagram

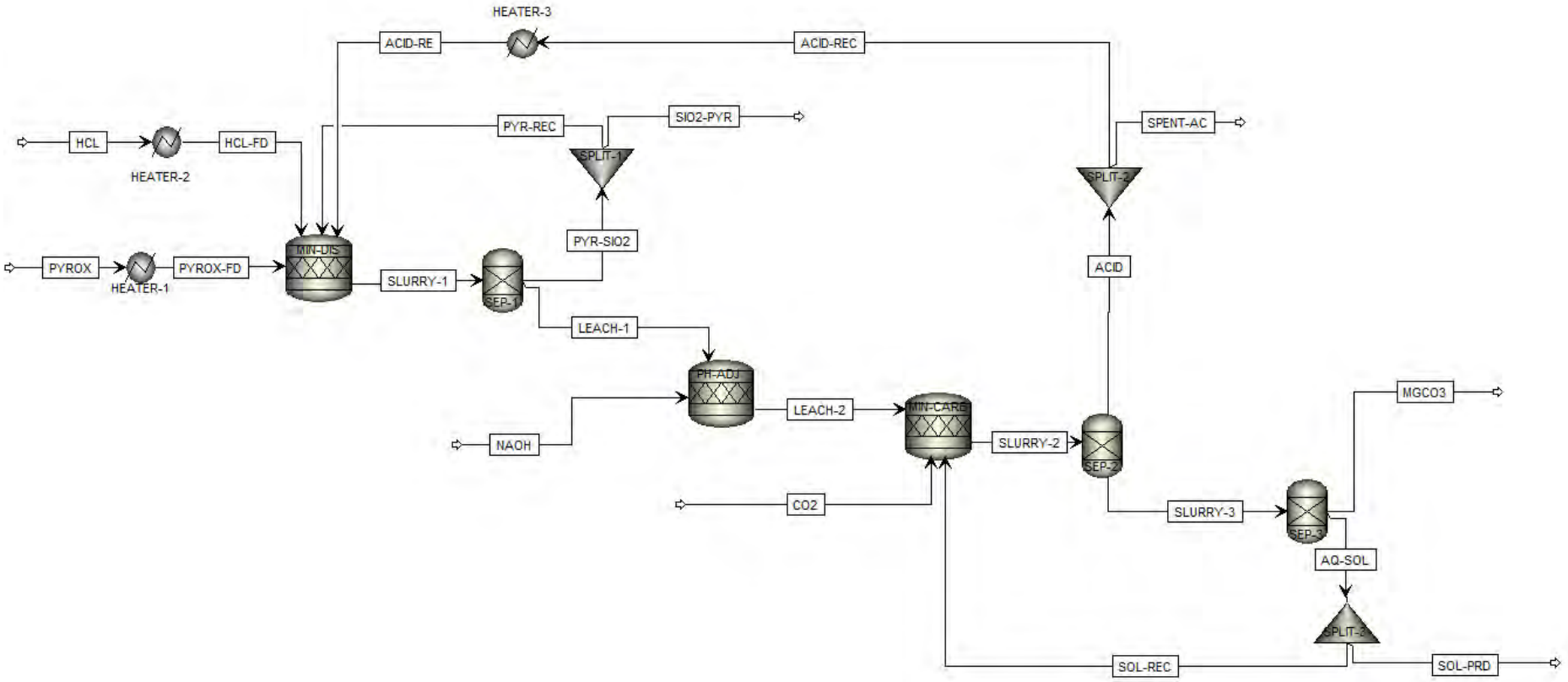

Figure E-4: Mineral acid pH swing process Aspen simulation diagram

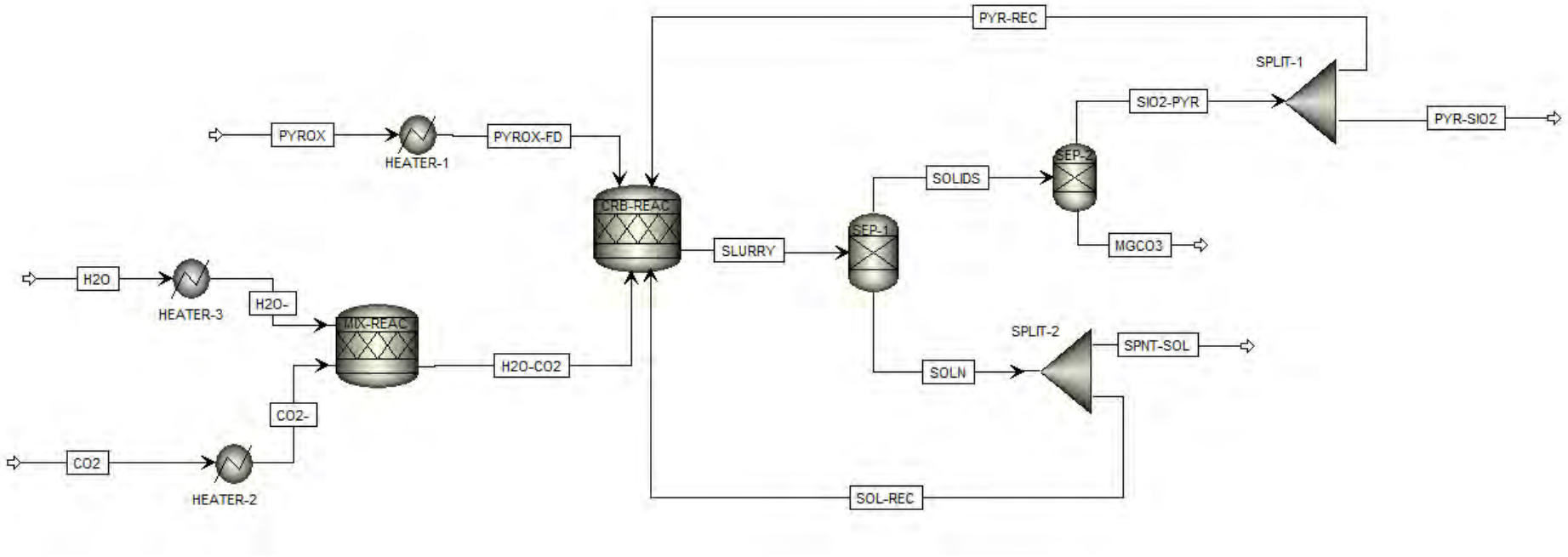

Figure E-5: Direct aqueous carbonation Aspen Plus simulation diagram

Additional Supporting Data

Table F-1: Net electricity requirements of selected mineral carbonation processes

Mineral Carbonation Process	Transport Compression (MJ/hr)	Electricity Credit (MJ/hr)	Net Electricity (MJ/hr)
Ammonium Salts	356.65	-141.93	214.72
Lackner's Multi-stage HCl	356.65	-141.93	214.72
Abo Akademi	356.65	-57.20	299.45
Mineral Acid pH Swing	356.65	-141.93	214.72
Direct Aqueous	356.65	50.89	407.53

Table F-2: Process carbon dioxide emissions burdens and contributions

Description	Carbon Dioxide Emissions Burdens (kg-CO_2e)				
	Ammonium Salts	**Lackner's HCl Multi-stage Process**	**Abo Akademi University**	**Mineral Acid pH Swing**	**Direct Aqueous**
Compression	60	60	84	60	115
Heat Requirements	7541	15677	1019	490	2116
Water	84	163	6	36	264
Reagent Make-up	1113	2394	232	570	2557
CO_2 Released	0	0	13	75	0
Total Burden	8798	18295	1354	1231	5052

Table F-3: The overall conversion of pyroxene in the selected mineral carbonation processes

Selected Process	Single Pass Conversion	Overall Conversion
Ammonium Salts	30%	68%
	50%	83%
	90%	98%
Lackner's Multi-Stage HCl	30%	81%
	50%	91%
	90%	99%
AAU Process	66%	95%
	100%	100%
Mineral Acid pH Swing	20%	56%
	30%	68%
	50%	83%
Direct Aqueous	5%	26%
	20%	71%