CARBON SEQUESTRATION THROUGH THE PRODUCTION OF PRECIPITATED CALCIUM CARBONATE FROM WASTE CONCRETE

by

Sterling Sherwood Slykhuis Vanderzee

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Abstract

As a result of human activities, rising concentrations of atmospheric carbon dioxide (CO$_2$) are causing climate change. One method to sequester CO$_2$ involves the production of synthetic limestone (CaCO$_3$) from calcium silicate minerals and CO$_2$ via mineral carbonation. Certain grades of CaCO$_3$, including Precipitated Calcium Carbonate (PCC), are sold as a filler and pigment to several industries. Therefore, if marketable as PCC, the production of CaCO$_3$ via mineral carbonation may be an economical method to help mitigate climate change. The global market for PCC offers the potential to utilize several million tonnes of CO$_2$ per year. Waste cement is a suitable source material for PCC production via mineral carbonation and can be recovered from waste concrete as a byproduct of aggregate recycling practices.

The objective of this research was to investigate the possibility of sequestering CO$_2$ by producing PCC via the recovery and carbonation of waste cement calcium. An acid (HCl) was used to allow the complete leaching of calcium, and so the dissolved calcium could be separated from the residual material via filtration to enable PCC recovery. A purification step via pH adjustment preferentially precipitated co-leached impurities such as iron and silicon. CaCO$_3$ precipitation was later induced by adding Na$_2$CO$_3$ that can be produced by the absorption of CO$_2$ from flue gases or the atmosphere (air capture) using NaOH. HCl and NaOH can be recycled via bipolar membrane electrodialysis. Although this method may require over twice the energy of the conventional PCC manufacturing process, low carbon electricity can be used and negative process emissions are currently feasible in multiple Canadian provinces. Lower energy carbonation methods could be used where stationary sources of concentrated CO$_2$ are located, however air capture is possible and the use of HCl and a purification step allows for the complete carbonation and utilization of waste cement calcium. This minimizes emissions from hauling residues and may ensure that significantly more CO$_2$ is absorbed by the waste cement than would otherwise be passively absorbed by the material over several decades of atmospheric exposure.
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Aragonite (CaCO₃)</td>
</tr>
<tr>
<td>AA/Ca ratio</td>
<td>Molar ratio of acetic acid added to calcium in the feedstock solids</td>
</tr>
<tr>
<td>ACC</td>
<td>Amorphous Calcium Carbonate (CaCO₃)</td>
</tr>
<tr>
<td>AEM</td>
<td>Anion Exchange Membrane</td>
</tr>
<tr>
<td>Alite</td>
<td>Ca₃SiO₅, 3CaO·SiO₂</td>
</tr>
<tr>
<td>Belite</td>
<td>Ca₂SiO₃, 2CaO·SiO₂</td>
</tr>
<tr>
<td>BMED</td>
<td>Bipolar Membrane Electrodialysis</td>
</tr>
<tr>
<td>BPM</td>
<td>Biopolar Membrane</td>
</tr>
<tr>
<td>C</td>
<td>Calcite (CaCO₃)</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>Calcium Chloride</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>Calcium Carbonate, Limestone</td>
</tr>
<tr>
<td>CaO</td>
<td>Calcium Oxide, Lime</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>Calcium hydroxide, Portlandite, Hydrated Lime</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon Capture and Storage</td>
</tr>
<tr>
<td>CEM</td>
<td>Cation Exchange Membrane</td>
</tr>
<tr>
<td>Cl₂(g)</td>
<td>Chlorine gas</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>CSR</td>
<td>Continuously Stirred Reactor</td>
</tr>
<tr>
<td>C-S-H</td>
<td>Hydrated Calcium Silicates</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethyl Ammonium Bromide</td>
</tr>
<tr>
<td>C&amp;D</td>
<td>Construction and Demolition</td>
</tr>
<tr>
<td>Dp</td>
<td>Diameter of Particles</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>EDAX</td>
<td>Name brand of Energy Dispersive Spectrometer</td>
</tr>
<tr>
<td>F₈₀</td>
<td>Passing size of 80% of the feed measured in µm</td>
</tr>
<tr>
<td>GCC</td>
<td>Ground Calcium Carbonate</td>
</tr>
<tr>
<td>GJ</td>
<td>Gigga Joules</td>
</tr>
<tr>
<td>Gt</td>
<td>Gigga tonnes</td>
</tr>
<tr>
<td>H₂(g)</td>
<td>Hydrogen gas</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>HCl:(Ca+Mg)</td>
<td>The molar ratio of HCl added to calcium + magnesium in the feedstock solids</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Induced Coupled Plasma Optical Emission Spectrometry</td>
</tr>
<tr>
<td>kW</td>
<td>kilowatts</td>
</tr>
<tr>
<td>kWh</td>
<td>kilowatt hours</td>
</tr>
<tr>
<td>Ksp</td>
<td>Solubility Product Constant</td>
</tr>
<tr>
<td>LCC</td>
<td>Low Carbonate Concrete</td>
</tr>
<tr>
<td>MJ</td>
<td>Mega Joules</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>Mt</td>
<td>Mega tonnes</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Sodium Bicarbonate</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>Sodium Carbonate</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>N/Ca ratio</td>
<td>Molar ratio of nitric acid added to calcium in the feedstock solids</td>
</tr>
<tr>
<td>P₈₀</td>
<td>Passing size of 80% of the product measured in µm</td>
</tr>
<tr>
<td>PCC</td>
<td>Precipitated Calcium Carbonate</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts Per Million</td>
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</tbody>
</table>
PHREEQC  A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations
RMC  Royal Military College of Canada
TGA  Thermogravimetric Analysis
V  Vaterite (CaCO₃)
W  Watts
Wᵢ  Bond’s Work Index
XRD  X-Ray Diffraction
Chapter 1

Introduction

1.1 Climate Change

The release of carbon dioxide (CO$_2$) from anthropogenic sources has a clear influence on the climate system (IPCC, 2013). A total of 34.5 billion tonnes (Gt) of CO$_2$ were emitted into the atmosphere from anthropogenic sources in the year 2012 (Olivier et al., 2013); for comparison this mass of CO$_2$ is over 20 times the mass of water in Lake Ontario, and equal to the mass of concrete produced world-wide in 2012.$^1$ By examining the geological record, it can also be seen that this rate of emission has no natural parallel in at least the last 300 million years of Earth’s history (Honisch et al., 2012); and from direct atmospheric measurement (the Keeling Curve), it can be seen that the concentration of CO$_2$ in the atmosphere has risen from 315 ppm in 1960 to 400 ppm in 2015 (Scripps, 2015). Policy makers have set a goal of reducing CO$_2$ emissions to such a level that global warming will be limited to, at most, an average of 2°C temperature rise by the year 2100. If anthropogenic emissions are not mitigated, an estimated $369 trillion in damages related to climate change have been predicted by 2200 as the result of damage to infrastructure, among other things (Hope and Schaefer, 2015). For reference purposes, the global economy in 2014 was nominally estimated at $77 trillion dollars (World Bank, 2015).

Additionally, urgent action to mitigate climate change is warranted because the Arctic is warming roughly twice as fast as the global average and the widespread thawing of Arctic permafrost is expected to release hundreds of billions of tonnes of CO$_2$ and billions of tonnes of methane into the atmosphere in what is known as a positive feedback loop (Hope and Schaefer, 2015). The manufacture of cement accounted for 9.5% of global CO$_2$ emissions in 2013 (Olivier et al., 2014).

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$^1$ 3.8 billions tonnes of cement were produced worldwide in 2012 (USGS, 2014); and concrete is typically 11% cement by mass (Portland Cement Associated, 2015)
1.5 Cement Manufacturing and Concrete

The CO$_2$ emissions from the cement manufacturing process are the result of combusting fossil fuels to heat limestone, clay, and sand to a temperature of 1450°C (≈40% of emissions); the transportation of raw materials (≈5%); and the production of electricity for manufacturing operations (≈5%). The remaining 50% of emissions are the result of the thermal decomposition of limestone (CaCO$_3$) to lime (CaO) and CO$_2$ (Mahasenan et al., 2003); these emissions cannot be mitigated by the use of alternative fuels, such as biomass. The lime reacts with molten sand in the kiln to form various calcium silicate phases:

$$2\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4 + 2\text{CO}_2 \quad T = 650-900^\circ\text{C} \quad (1.1)$$

$$\text{Ca}_2\text{SiO}_4 + \text{CaO} \rightarrow \text{Ca}_3\text{SiO}_5 \quad T = 1300-1450^\circ\text{C} \quad (1.2)$$

The product of a cement kiln is termed clinker, which is ground with appropriate additives such as gypsum and limestone to form cement; the most widely used type of cement type is Portland cement which consists of 95% clinker by mass. The energy required for clinker production varies from 3-6 GJ per tonne of clinker for different technologies (equivalent to 830-1660 kWh/tonne); the thermodynamic minimum to drive the endothermic reactions is ~1.8 GJ per tonne of clinker, however this assumes a dry limestone feedstock and the energy requirements are much higher for feedstocks with high moisture content (IEA, 2007).

Cement typically accounts for 11% of the mass of concrete, the remainder consists of coarse aggregates (41%), fine aggregates (26%), water (16%) and entrained air (6%) (Portland Cement Association, 2015). The calcium content of cement is approximately 46.5% by mass (reviewed in Tam et al., 2007) and therefore 5.1% of concrete. The composition of cement and concrete are shown schematically in Figure 1.1.
Figure 1.1: The composition of cement and concrete.

Alite (Ca$_3$SiO$_5$ or 3CaO·SiO$_2$) is the primary component of cement and it provides concrete with cohesive strength after it reacts with water to form an amorphous calcium silicate hydrate (C-S-H) phase and calcium hydroxide (Lea, 1998, p. 243):

\[ 3\text{CaO} \cdot \text{SiO}_2 + (3 + m - n)\text{H}_2\text{O} \rightarrow n\text{CaO} \cdot \text{SiO}_2 \cdot m\text{H}_2\text{O} + (3 - n)\text{Ca(OH)}_2 \]  (1.3)

1.2 Carbon Capture and the Cement Industry

In addition to mitigating CO$_2$ emissions by reducing the consumption of fossil fuels, Gasser et al. (2015) have predicted that even with very high mitigation rates, at least 1.8-11.0 Gt of CO$_2$ will have to be captured and stored per year if global warming is going to be limited to less than 2°C by 2100. This amounts to up to one third of current global CO$_2$ emissions. The cement industry is an attractive target for carbon capture and storage (CCS) because it accounted for approximately 9.5% of global CO$_2$ emissions in 2013 (Olivier et al., 2014) and approximately half the emissions are from limestone decomposition (Mahasenan et al., 2003).

The cement industry also has the potential to achieve negative emissions (i.e. actively remove CO$_2$ from the atmosphere and become an industrial-scale carbon sink). This can be achieved through the combined implementation of conventional CCS technologies and mineral
carbonation throughout the renewal cycle of infrastructure (Figure 1.2). Conventional CCS technologies can separate CO₂ from the flue gas of the cement manufacturing plant and store the CO₂ underground (IPCC, 2005). Mineral carbonation can sequester CO₂ through the conversion of uncarbonated calcium minerals (found in cement) to calcium carbonate (CaCO₃). The carbonation of cement occurs in several steps in the aqueous phase (Katsuyama et al., 2005), however it can be summarized as follows:

\[ 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O(s)} + 3\text{CO}_2(g) \rightarrow 3\text{CaCO}_3(s) + 3\text{H}_2\text{O} + 2\text{SiO}_2(s) \]  
\[ \text{(1.4)} \]

\[ \text{Ca(OH)}_2(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O} \]  
\[ \text{(1.5)} \]

The cement phases can be partially recovered in a byproduct (waste fines) from currently existing facilities that produce recycled aggregates by crushing waste concrete. The recycled aggregates are used in road construction and are also blended into new concrete, particularly if they are treated to remove the cement component (CSI, 2009 and Iizuka, 2006). Also of interest is that certain grades of CaCO₃, such as Precipitated Calcium Carbonate (PCC), have several industrial applications. Therefore the product of sequestering CO₂ via mineral carbonation might be sold to sustain the implementation of this process if it can be separated from other components of the source material. Once the demand for industrial grade CaCO₃ is met, the remaining supply of waste cement might be carbonated by slower and less energy intensive methods that do not necessarily separate marketable CaCO₃ from the other components of the source material. Such carbonation methods have been studied with other types of alkaline industrial waste (Harrison, Power and Dipple, 2012).
Figure 1.2: The sequestration of CO₂ through the renewal cycle of infrastructure (~60 yrs).

It should be noted that if the CaCO₃ produced via cement carbonation is recovered separately from the residues, it could also be recycled as cement kiln feed. This would offset the emissions from virgin limestone and cement production facilities might be relocated closer to urban areas where the cement is used, rather than where suitable natural deposits of limestone are located. However, the costs of producing suitable CaCO₃ via mineral carbonation would likely exceed the value of the cement. In one of the lower energy consumption scenarios where CO₂ is removed from the flue gas of a thermal power plant via amine-scrubbing, and waste heat is used to release of absorbed CO₂ for pressurization and calcium leaching, CaCO₃ recovery was estimated to cost at least $136 U.S. per tonne of CaCO₃ (Katsuyama et al., 2005). Since cement was valued at approximately $100 U.S. per tonne of cement between 2007 and 2015 (Statista, 2016) and cement contains about 46.5% calcium, $158 worth of CaCO₃ would be required to make $100 worth of cement before even considering other production costs. Carbon credits would need to be at least $310/tonne CO₂ to cover the added cost producing CaCO₃ via mineral carbonation if it assumed that the avoided costs of sourcing and crushing limestone (the conventional practice) are negligible. Furthermore, an urban cement production plant is unlikely to create sufficient savings in transportation costs to offset the added costs of producing CaCO₃ via mineral carbonation
because the World Bank (2016) estimated the costs of transportation to a site 100 km and back by truck trailer to be approximately $6 per tonne of cargo.

1.4 Waste Concrete Generation and Recycling

Concrete buildings have a typical lifetime of 50-60 years, and the records on global cement production (Figure 1.3) suggest that the current global scale of waste concrete generation is only a fraction of what it will be in the next 50-60 years. Since 3.8 billion tonnes of cement were produced in 2012, up to 2.0 billion tonnes of CO$_2$ could be sequestered from that year’s production if all the waste cement is carbonated as part of a waste concrete recycling process$^2$. In the U.S., the rate of cement production has been relatively stable since the mid 1960’s at ~70 million tonnes of cement per year, and the current sequestration potential could be ~35.8 million tonnes of CO$_2$ per year. From Figure 1.1, this amounts to over 600 million tonnes of concrete that will become waste once the structures are demolished. The World Business Council on Sustainable Development recently reported that over 900 million tonnes of waste concrete were generated per year in Europe, the US and Japan alone, with unknown quantities elsewhere (CSI, 2009).

![Figure 1.3: The history of cement production (Gt per year) from 1926-2012. Data retrieved from USGS (2014).](image)

$^2$ Since cement is ~46.5% uncarbonated Ca, and ~44g of CO$_2$ can be removed by 40g of Ca because CaCO$_3$ is produced.
Waste concrete recycling practices currently exist, and some countries (e.g. Japan and the Netherlands) achieve a near perfect recovery of waste concrete (CSI, 2009); however they do not include a waste cement carbonation step. The aggregate component is generally what is valued, while the cement component is typically seen as a problem or is not specifically desired in the recycled product.

In Ontario, recycled waste concrete aggregate is used in road construction or as backfill material, and comprehensive set of material specifications have been developed and maintained to regulate this use (OPSS.MUNI 1010). The rate of waste concrete production is such the recycling yards will soon reach full capacity, and while diversion from landfill is important, the main policy drivers for waste concrete recycling in Ontario are the opposition to new aggregate operations by the public, and demand for broader sustainable development, including lower CO₂ emissions (Messerschmidt, 2013). The mitigation of transportation costs and landfill fees is also a strong driver for contractors to send waste concrete to recycling yards. In Japan and the Netherlands, an almost perfect waste concrete recycling rate is achieved mostly through applications in road construction (CSI, 2009); however a surplus of waste concrete is expected in the near future (Nakagawa et al., 2005). Some jurisdictions, particularly those concerned with resource security and depleting dumping sites also permit the use recycled concrete to replace natural coarse aggregates in new concrete; regulations in Hong Kong allow for a 30% replacement (Tam et al., 2007).

The main property of recycled aggregate that limits its application in new concrete is its high porosity and high rate of water absorption (wt%/min), which is derived from the hydrated cement adhered to the natural aggregate. This creates a weaker interfacial zone between the new cement and aggregates, and also exacerbates freeze-thaw damage (Tam et al., 2007). In order to permit a higher percentage of recycled aggregate in new concrete, several methods have been investigated to remove the hydrated cement component from recycled aggregate through
mechanical, thermal, and chemical means (Nakagawa et al., 2005; Sima et al., 2005; Iizuka et al., 2010; Tam et al., 2007; Akbarnezhad et al., 2011). With all of these methods the cement component is incorporated into a finely crushed (<5mm) or aqueous byproduct of high-quality recycled aggregate production. Additionally, Lafarge (2014) reported that the fine particles (<5mm) represent approximately a third of production when manufacturing recycled aggregates (5-25mm) from waste concrete without a specific treatment step to remove the adhered cement. It was also reported that these fines are difficult to sell on their own, and often need to be discarded when manufacturing drainage stone (also known as “clears”).

Waste concrete fines are therefore essentially a by-product from both the production of road construction materials and recycled aggregate for new concrete, and the smallest particle size fractions (<500µm) have been found to have a high cement content (Florea and Brouwers, 2012; Shuto et al., 2014 and Iizuka, 2006). This means that a finely ground material composed of up to ~30% wt. uncarbonated calcium can be recovered as a byproduct from current waste concrete recycling practices without any additional crushing or grinding (Shuto et al., 2014); thus it is an attractive material to use for carbon sequestration.

It should be noted that cement will passively absorb some CO$_2$ throughout its lifetime. This “passive carbonation” progresses inwards from exposed surfaces and the carbonation depth is proportional to the square root of exposure time. The carbonation rate is controlled by the formation and diffusion of carbonate ions towards the interior of the material, therefore the exposure conditions play a significant role (Pade and Guimaraes, 2006). After 50 years of exposure to atmospheric conditions, the depth of carbonation is typically limited to a few centimeters from the surface of the concrete (Iizuka, 2006 and Flower and Sanjayan, 2007). Although passive carbonation can be promoted after demolition through crushing to create more exposed surface area (Pade and Guimaraes, 2006), there may not be sufficient exposure time for passive carbonation to fully carbonate the cement. This is because after shortly crushing, the
materials will likely become either encased in new concrete, compacted and covered by asphalt in road construction, or piled at a landfill. Furthermore, additional motives for recycling waste concrete are needed (Messerschmidt, 2013; Nakagawa et al., 2005).

1.6 Industrial Calcium Carbonate

Multiple grades of CaCO$_3$ have industrial applications, and are valued at up to $500 US per tonne (Roskill, 2012). Roskill estimated that in 2011 approximately 74 million tonnes of industrial grade CaCO$_3$ were consumed, therefore CaCO$_3$ production from waste could provide economic support to sequester ~32.6 million tonnes of CO$_2$ per year (CaCO$_3$ is 44% CO$_2$ by mass). Sequestering this much CO$_2$ per year would be equivalent to taking 6.9 million passenger vehicles off the road annually, equivalent to 0.68% of cars globally.

Out of the 74 million tonnes of calcium carbonate (CaCO$_3$) used globally in 2011, 60 million tonnes was accounted for by ground calcium carbonate (GCC), and the remaining 14 million tonnes consisted of precipitated calcium carbonate (PCC). GCC is more widely used because it is less expensive to make and is more readily available, while PCC is more valuable and versatile because its morphology, particle size, particle size distribution and brightness can be controlled during its production.

The conventional PCC production method involves thermally decomposing limestone in a 900°C kiln to make CaO and CO$_2$ (Teir et al., 2005). The CaO is added to water to produce a Ca(OH)$_2$ slurry, which is then screened to remove coarse particles, and then a CO$_2$ rich gas is bubbled through the screened slurry to precipitate CaCO$_3$ (Oates, 1998). The net CO$_2$ emissions are due to the combustion of fossil fuels to heat the limestone. Teir et al. (2005) calculated that this process requires 2,244 MJ (equivalent to 623 kWh) of thermal energy to produce one tonne of CaCO$_3$, and that it produces 210 kg of CO$_2$ per tonne of CaCO$_3$ when heavy fuel oil is used.

---

3 The average CO$_2$ emissions for a passenger vehicle are 4.7 tonnes per year (EPA, 2014).
4 1.015 billion cars globally in 2010 (Sousanis, 2011).
This is the primary method used in North America to produce PCC (Roskill, 2012). Therefore, in addition to sequestering CO$_2$, an alternative production method could also mitigate up to 210 kg of CO$_2$ per tonne of PCC. In an idealized scenario (assuming no passive carbonation or electricity emissions), net negative process emissions of 650 kg of CO$_2$ per tonne CaCO$_3$ are possible (210 kg mitigated + 440 kg sequestered). Other emission reduction pathways might also be possible through the production of recycled aggregates and recycled sand from waste concrete, such recycling processes have been studied by other authors (Iizuka et al., 2010).

The paper industry is the largest market for calcium carbonate, where it is used as a filler and coating pigment in paper. It accounted for approximately 32% of GCC and 73% of PCC consumption in 2011 (Roskill, 2012). Both paper recycling facilities and pulp and paper mills produce a waste sludge that contains CaCO$_3$; these waste products are typically landfilled but are sometimes incinerated before-hand to reduce the mass of waste (de Alda, 2008). If incinerated at temperatures above 600ºC, any CaCO$_3$ made by cement carbonation would likely release its stored CO$_2$, however CO$_2$ emission reductions are still possible because CO$_2$ would otherwise be released from CaCO$_3$ made directly from virgin limestone (CaCO$_3$). In other words, if CO$_2$ is released from CaCO$_3$ made via the carbonation of cement, the net emissions are considered zero because the calcium reverts back to its original state of being uncarbonated. Therefore at the very least emission reductions come from avoiding the calcination of PCC made directly from virgin limestone and from using an electrochemical process with low carbon energy rather than a thermal process with fossil fuels.

1.3 Objective of this Thesis

The objective of this thesis is to investigate a process that sequesters CO$_2$ through the production of potentially marketable PCC from waste concrete. The method of interest involves the recovery of cement from waste concrete by utilizing waste fines and the leaching of calcium by HCl, along with CO$_2$ capture by NaOH solution. Waste fines are defined as particles of
crushed waste concrete that are recovered as a byproduct from crushing waste concrete into recycled aggregates. The main reagents (NaOH and HCl) can be regenerated from the resultant NaCl solution via electrochemical methods, thus recycling reactants. The schematic for the process is shown below in Figure 1.4.

![Figure 1.4: Process schematic of the HCl/NaOH waste concrete recycling process.](image)

The process consists of six main steps:

1) Waste concrete fines are recovered as a by-product from crushing waste concrete into coarse recycled aggregates. Depending on the aggregate composition and crushing methods, the fines can contain various proportions of calcium compounds such as Ca(OH)$_2$, 3CaO·2SiO$_2$·3H$_2$O, CaCO$_3$, CaMg(CO$_3$)$_2$, with other minor components.

2) The calcium in the cement portion of waste concrete fines is then dissolved by hydrochloric acid:

$$3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}(s) + 6\text{HCl}(aq) \rightarrow 3\text{CaCl}_2(aq) + 2\text{SiO}_2(s) + 6\text{H}_2\text{O}$$  \hspace{1cm} (1.6)

3) The resultant solution is purified by increasing the pH through the addition of alkalinity. The impurities most likely precipitate as amorphous silicates rather than hydroxides. This
4) CO₂ is removed from a gas stream in an absorption tower using a sodium hydroxide solution. Packing materials can be used to increase the rate at which CO₂ is absorbed into the solution by increasing the gas-solution contact surface area.

\[
2\text{NaOH}(aq) + \text{CO}_2(g) \rightarrow \text{Na}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l)
\]

5) Calcium carbonate is precipitated by mixing the calcium chloride solution with the carbonate-containing solution produced in the CO₂ capture step:

\[
\text{CaCl}_2(aq) + \text{Na}_2\text{CO}_3(aq) \rightarrow \text{CaCO}_3(s) + 2\text{NaCl}(aq)
\]

6) The residual sodium chloride solution is recycled back into sodium hydroxide and hydrochloric acid through bipolar membrane electrodialysis (BMED). Membrane electrolysis (used in the chlor-alkali industry) was considered to regenerate NaOH and HCl, but BMED may be better suited because it requires less energy, can use dilute salts as input, and does not produce chlorine gas. The parenthesis in the following equation are used to illustrate that NaOH and HCl are physically separated by membranes to prevent neutralization.

\[
\text{NaCl}(aq) + \text{H}_2\text{O} \rightarrow \{\text{NaOH}(aq)\} + \{\text{HCl}(aq)\}
\]

Ideally the only input materials for the process are the waste concrete fines, CO₂ and possibly a small amount of alkalinity (e.g. calcium hydroxide or lime). The output materials are CaCO₃ along with residual fines and potentially a purification residue. Both the residual fines and purification residue likely require washing to recover chlorides.

The experiments in this thesis are focused on characterizing the waste concrete fines produced in a laboratory setting (step 1), calcium leaching from the fines (step 2), removal of
impurities from solution (step 3), and precipitation of CaCO$_3$ through the addition of Na$_2$CO$_3$ (step 5). The remaining steps were not investigated, but they have been studied by other authors (Zeman, 2007) (step 4) and Shuto et al., 2014 and 2015 (step 6). The net process and transportation emissions are estimated through values obtained in the literature.
Chapter 2

Literature Review

2.1 Recycling Waste Concrete

This section of the literature review covers a broad array of topics that are within the scope of waste concrete recycling. The materials, methods, and accepted recycling practices are reviewed, as well as some of the main motives for recycling. The performance of conventional aggregate production facilities and road transport are also included. Finally, the passive carbonation of concrete is reviewed.

2.1.1 Waste Concrete Materials for Carbon Sequestration

The CO$_2$ sequestration potential of waste concrete materials is defined by the fraction of cement calcium that is not carbonated (uncarbonated calcium). Considering the contribution from cement alone, unprocessed waste concrete should contain approximately 5.1 wt% uncarbonated calcium before the composition of the aggregate is considered (Figure 1.1), however, an interesting by-product of recycled concrete aggregate production was described by Iizuka (2006). It was termed “waste cement” and was defined as a fine powder (~200µm diameter) containing mostly hydrated cement and some finely crushed aggregate that is recovered after crushing waste concrete. It was found to contain ~27 wt% calcium (~24% uncarbonated calcium, and ~3% carbonated calcium); this material was used for CO$_2$ sequestration through mineral carbonation (Iizuka, 2006). More recently, Shuto et al. (2014) recovered “waste cement” from an aggregate recycling facility where waste concrete was crushed and then sieved to classify the particles (40-200 mm, 5-40 mm, and <5 mm in diameter). The waste cement was recovered by separating the <212 µm fraction, which contained 32% calcium by weight. Most of this calcium was believed to be uncarbonated and associated with hydrated cement. The mass of
waste cement recovered per tonne of concrete was not reported, and the <5 mm fraction was described as byproduct with no current use.

2.1.2 Methods to Produce Recycled Aggregate from Waste Concrete

There are several methods to remove the adhered cement from recycled aggregates for use in new concrete: a mechanical crushing and grinding method, and a heating and grinding method (Iizuka, 2006; Nakagawa et al., 2005; Sima et al., 2005; and Iizuka et al., 2010). Other methods use various types of acids to dissolve the cement, or use microwaves to create thermal stress to break the hydrated cement and aggregate apart (Iizuka et al., 2010; Tam et al., 2007; Akbarnezhad et al., 2011).

2.1.2.1 Mechanical Crushing and Grinding

The mechanical crushing and grinding method involves crushing the waste concrete and separating the coarse aggregates (5-40mm); the remaining fine aggregates (<5mm) cannot be reused in new concrete because the hydrated cement component is too difficult to remove from the fine aggregate by crushing alone. After crushing, the coarse aggregates account for 80% of the original mass, and the fine aggregates account for 20% (Iizuka, 2006). Additional grinding of the coarse aggregate is done to remove more of the hydrated cement, and this can reduce the coarse aggregate component to ~30% of the original mass (i.e. ~25% of the original coarse aggregates are crushed into fines if the original coarse aggregate content of concrete is ~40%). The below 5mm fraction therefore accounts for ~70% of the original mass, and contains the waste cement. Two organizations were said to utilize this technique in Japan (Iizuka, 2006).

2.1.2.2 Heating and Grinding

In the heating and grinding method, both coarse and fine aggregates can be recycled because the hydrated cement is removed from the aggregates by heating to 300-400°C. The mechanism for this process is the dehydration of hydrated cement components (C-S-H and
Ca(OH)$_2$, causing deterioration of the interface between the hydrated cement and the aggregate (Shima et al., 2005; Iizuka, 2006; Butler et al., 2011). This is consistent with Zimbelmann (1985), who found that calcium hydroxide is present mainly at the aggregate/hydrated cement interface, and that calcium hydroxide is mainly responsible for the cement-aggregate bond. Butler and colleagues (2011) also found that the thermal method proved more effective at removing hydrated cement than nitric acid dissolution or freeze-thaw methods. Presoaking the recycled aggregates prior to heating can increase the efficiency of this method by increasing thermal stresses, and so can immersing the heated recycled aggregates in cold water (De Juan and Gutierrez, 2009).

A waste concrete recycling pilot plant utilizing the heating and grinding method was constructed and 300°C was selected as the optimal temperature (Shima et al., 2005). The output was described as 35% coarse aggregate (5-40mm), 30% fine aggregate (<5mm), and 35% fine powder (waste cement). The electricity and fuel consumption per tonne of waste concrete input was listed as 3.0 kWh of electricity for concrete crushing, 93 kWh from kerosene for heating\(^5\), 26.0 kWh of electricity for grinding and aggregate recovery (a vibrating screen separated aggregates by particle size), and 7.3 kWh from light oil for heavy equipment operation\(^6\) (Shima et al., 2003). Therefore this process requires 130 kWh/t concrete, and is summarized in Figure 2.1. By accepting the carbon intensity of kerosene and fuel oil as 0.26 and 0.28 kg CO$_2$/kWh respectively, the emissions amount to 26.2 kg CO$_2$/tonne concrete plus the emissions from the remaining 29.0 kWh/t concrete of electricity. If this method was used to recover 100% of the cement from waste concrete for CO$_2$ sequestration through mineral carbonation, then the

\(^5\) Converted from 7.8 kJ kerosene at 43.1 MJ/kg kerosene
\(^6\) Converted from 0.8 kg light oil at 44 MJ/kg light fuel oil
emissions from the hydrocarbon fuels alone would deplete the net CO₂ sequestration capacity of waste concrete by over 50%\(^7\).

Figure 2.1: Summary of the heating and grinding method.

Iizuka (2006) reviewed this process, and mentioned that at the time this technique was still at the research stage due to its high energy use and associated cost. For comparison with conventional aggregate production methods, Flower and Sanjayan (2007) found that production of coarse aggregates from granite required 26.4 kWh for crushing (electricity) plus 34.0 kWh/t for excavation, hauling and transport off site (diesel). Additionally, the authors found the production of fine aggregates (sand) to require 4.8 kWh/t for screening (electricity) and 26.6 kWh/t for strip mining and transport off site (diesel)\(^8\). Therefore, if the heating and grinding method requires 130 kWh to produce 0.35t coarse aggregate 0.3t fine aggregate (Figure 2.1), and conventional aggregate production requires 60.4 kWh/t for coarse aggregates and 31.4 kWh/tonne for fine aggregates, then the heating and grinding method consumes over four times the energy required to produce the aggregates (0.35t coarse and 0.3t fine) by conventional methods. This includes the energy required for transporting the conventionally produced (i.e. virgin) aggregates, although the

\(^7\) If waste concrete contains 5% uncarbonated calcium by mass, then 55kg CO₂ can be sequestered per tonne of waste concrete (with a perfect cement recovery efficiency).

\(^8\) Converted from 2.4 L diesel per tonne of sand at 11.1kWh/L diesel
average transportation distance was not specified in Flower and Sanjayan (2007), and excludes the energy for transporting the recycled aggregates since recycled aggregates are more likely to be produced close to where they are needed.

2.1.2.3 Acid Treatment

Carbonic acid in conjunction with ball mill treatment has been used to remove the waste cement from the fine aggregates composed of SiO$_2$, i.e. quartz sand (Iizuka et al., 2010). In this method the calcium is dissolved under high pressure CO$_2$ and then later precipitates as CaCO$_3$ in a separate reactor once the CO$_2$ pressure is reduced. The ball mill treatment was done to remove a fragile but porous residue from the fine SiO$_2$ aggregates.

Other acids such as hydrochloric, sulfuric, and phosphoric acid have been used to remove hydrated cement from coarse aggregates (Tam et al., 2007). The hydrochloric approach was found to reduce the water adsorption of recycled aggregates (RA) without exceeding the limit for chloride content (0.05%) after acid treatment and washing; furthermore the compressive strength, flexural strength and modulus of elasticity were found to improve when compared to those using traditional approaches (Tam et al., 2007). The authors also provided as summary of previous research on recycled aggregate performance (Annex I), which shows the strength of concrete made with various proportions of recycled aggregate.

2.1.2.4 Microwave Treatment

Akbarnezhad et al. (2011) studied the removal of hydrated cement from recycled aggregates by using microwaves to take advantage of different material properties (granite aggregates were used). The microwaves were explained to create a thermal expansion gradient that exfoliation the hydrated cement from the aggregate. Differences in porosity (i.e. water content) between the hydrated cement and granite may be the most important material property difference that caused the hydrated cement to expand more than the granite. The authors found that with ~1.2 minutes of microwave heating, 32% of the mortar could be removed and when the
aggregates were immersed in water before microwave treatment up to 48% of the mortar was removed. The authors also tested the heating method and found that 13% of the mortar was removed after 120 minutes of treatment at 500°C. The results were due to faster and more concentrated heating of the mortar by the microwaves, resulting in a higher differential thermal stress in the mortar; whereas with the conventional heating method the mortar and aggregate gradually heated to the same temperature (since microwaves heat from the center out vs. radiant heat, which is outside in). They also found that on its own mechanical grinding could remove 28% of the mortar after 6 minutes; when mechanical grinding was used in combination with microwave treatment 85% of the mortar was removed from presoaked recycled aggregate. Mechanical grinding used in combination with conventional heating at 500°C removed 55% of the mortar from non-presoaked recycled aggregate. The authors also determined that the incorporation of up to 40% microwave-treat recycled aggregate had a “negligible effect” on the mechanical properties of concrete. The energy consumed by these various methods was not quantified.

2.1.3 Recycling Concrete as Roadbed Material

Using crushed waste concrete as roadbed material is the most widely accepted method of concrete recycling. The waste concrete is processed by crushing and classifying, and the output material consists of 80% “recycled stone” (5-40mm) and 20% “recycled sand” (<5mm); both size fractions are used as roadbed material. If the waste concrete is processed at a C&D site, both size fractions are used as backfill material in Japan according to Iizuka (2006). Recycled aggregates also have the potential to be used in asphalt pavement (Messerschmidt, 2013). The Netherlands and Japan achieve an almost complete recovery of waste concrete through reuse as roadbed material, and the coarse recycled aggregates are believed to more suitable than virgin aggregates for road base and sub-base because recycled aggregates often have better compaction properties
(CSI, 2009). In Ontario up to 100% recycled concrete can be used as road base and sub-base (Messerschmidt, 2013).

It should be noted that while Japan had a waste concrete recycling rate of 96% in 2000, a surplus of waste concrete was anticipated in the near future due to the demolition of buildings built during the 1970’s, their period of high economic growth, along with a shortage of dumping yards, and diminished aggregate resources (Nakagawa et al., 2005). While diversion from landfill is important, the main policy drivers for waste concrete recycling in Ontario are the opposition to new aggregate operations by the public, demand for broader sustainable development, lowering CO$_2$ emissions and a social license for the aggregate industry (Messerschmidt, 2013). The amount of CO$_2$ emissions avoided by using recycled aggregate is mostly dependent on reducing fugitive emissions associated with transportation, which is location specific (Figure 2.2). Within the Greater Toronto Area there is a cluster of recycled aggregate production facilities near the downtown core, providing a logistical advantage compared to virgin aggregate sources (Lafarge, 2014).

2.1.4 Transportation

Eloneva et al. (2012) reviewed that the CO$_2$ emissions associated with transporting materials by truck and trailer are 1.335 kg CO$_2$ per km with a full load (40 tonnes) and 0.879 kg CO$_2$ per km when empty. Therefore, the emissions from transportation can be estimated to be 5.535 kg CO$_2$ per 100 km between sites (200 km round trip) per tonne of cargo. Since the carbon intensity of diesel is 0.27 kg CO$_2$/kWh, transportation consumes an estimated 20.5 kWh per 100 km between sites (200 km round trip) per tonne of cargo. From an economic perspective, the cost of transporting goods by truck and trailer is between $4-6$ U.S. per 100 km per tonne of cargo when the terrain is predominantly flat (World Bank, 2016). The cost of fuel was found to account for 20-30% of the transportation cost, the remainder of which was accounted for by maintenance materials (26-40%), labor (15-25%), depreciation and interest (15-20%), overheads and other
costs (10-15%). Of note is that at the present time there are several gas-fired power plants in the Toronto area that are in close proximity to waste concrete aggregate recycling facilities (IESO, 2016 and Larfarge, 2014).

Table 2.1: Transporting materials by truck and trailer.

| The Emissions and Requirements for the Transportation of Materials by Truck and Trailer |
|----------------------------------|-------------------------------|-----------------------------|
| 5.535 kg CO\textsubscript{2} emitted tonne \cdot 100 km between sites | 20.5 kWh consumed tonne \cdot 100 km between sites | $4 – $6 U.S. tonne \cdot 100 km between sites |

With respect to the transportation requirements for conventional PCC production methods, a high purity limestone is used as input (Roskill, 2012), therefore the proximity of these deposits to the production facility and the user can have a significant influence of the life cycle emissions and cost of PCC. Eloneva et al. (2012) reviewed that Finland imports limestone from France and Norway for PCC production, where the transportation distance between Paris, France and Helsinki, Finland is approximately 2,500 km (emitting 138 kg CO\textsubscript{2} and costing up to $150 U.S. per tonne of PCC). There may be other regions that import materials from a similar distance. Also, Teir (2008) reviewed that Finland also does not have any suitable geological formations for CO\textsubscript{2} storage, and that transporting CO\textsubscript{2} by pipeline costs 1-8 $US/t CO\textsubscript{2} per 250 km.

2.1.5 Energy Requirements for Crushing and Pulverization

In order to estimate the total energy requirements for PCC production from waste concrete, the energy required for crushing should be included. Legendre and Zevenhoven (2014) reviewed that the energy efficiency of comminution (particle size reduction) equipment is typically under 10% because input power is dissipated as heat, noise and in ineffective material deformation. Bond’s equation can be used to estimate the energy requirements for crushing, grinding and milling; the equation factors in how readily a specific material is comminuted, and
the initial and final size of 80% of the particles. Yan and Gupta (2006) showed that Bond’s equation can be written as:

\[ E = 10W_i \left[ \frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right] \]  

(2.1)

Where  

- \( E = \text{kWh/t} \)
- \( P_{80} = \text{80\% passing size of the product in microns} \)
- \( F_{80} = \text{80\% passing size of the feed in microns} \)
- \( W_i = \text{the Bond Work Index for particular rock type.} \)

The Bond Work Index \((W_i)\) is experimentally determined and represents the work required to reduce the rock to 100\(\mu\)m (kWh/tonne). The \(W_i\) for various materials are listed in Table 2.2 (Yan and Gupta, 2006; Konstantinos, 2015). For example, the electrical energy required to pulverize limestone \((W_i = 11.7 \text{ kWh/tonne})\) boulders \((F_{80} = 50 \text{ cm})\) to a fine powder \((P_{80} = 5 \mu\text{m})\) is approximately 52 kWh/tonne. This value might be representative of the energy required to pulverize a tonne of limestone into ground calcium carbonate (GCC).


<table>
<thead>
<tr>
<th>Material</th>
<th>Work Index (kWh/tonne)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basalt</td>
<td>18.85</td>
<td>1</td>
</tr>
<tr>
<td>Cement Clinker</td>
<td>14.95</td>
<td>1</td>
</tr>
<tr>
<td>Cement (raw)</td>
<td>11.59</td>
<td>1</td>
</tr>
<tr>
<td>Dolomite</td>
<td>12.42</td>
<td>1</td>
</tr>
<tr>
<td>Gneiss</td>
<td>22.19</td>
<td>1</td>
</tr>
<tr>
<td>Granite</td>
<td>16.6</td>
<td>2</td>
</tr>
<tr>
<td>Limestone</td>
<td>11.7</td>
<td>2</td>
</tr>
<tr>
<td>Quartzite</td>
<td>17.4</td>
<td>2</td>
</tr>
<tr>
<td>Syenite</td>
<td>14.47</td>
<td>1</td>
</tr>
</tbody>
</table>

**2.1.6 Conventional Aggregate Production for Concrete**

Flower and Sanjayan (2007) studied the performance of coarse and fine aggregate production facilities in Australia; coarse aggregates were produced through blasting, excavating crushing, and screening rock, while fine aggregates (sand) were produced through strip mining and screening. The authors found that the coarse aggregate production facilities consumed 26.4 kWh of electricity per tonne of granite aggregate, plus 34.0 kWh of diesel per tonne for excavation, hauling and transport off site. Additionally, the authors found the production of fine
aggregates (sand) to require 4.8 kWh per tonne of electricity and 26.6 kWh per tonne of diesel for strip mining and transport off site\(^9\). Therefore coarse aggregate production required a total of 60.4 kWh/t, and fine aggregate production required 31.4 kWh/t. The emissions from diesel alone amount to 16.3 and 8.5 kg CO\(_2\) per tonne of coarse and fine aggregates, respectively\(^{10}\). The average distance between the production facilities and the users was not specified.

The real-world result of 26.4 kWh of electricity per tonne of coarse granite aggregate (Flower and Sanjayan, 2007) is significantly greater than that which would be estimated with Bond’s equation. Equation 2.1 estimates that only 1.5 kWh are required to crush granite (\(W_i = 16.6 \text{ kWh/tonne}\)) from boulders 2m in diameter to 10 mm in diameter. The difference between the two values is speculated to be due to equipment inefficiencies (Legendre and Zevenhoven, 2014). Still, Bond’s equation has been used to estimate the energy requirements for crushing and pulverization (Kakizawa et al., 2001; Kodama et al., 2008; Teir et al., 2005).

### 2.1.7 Passive Carbonation

A portion of cement will passively carbonate throughout the lifecycle of concrete. Collins (2010) stated that if passive carbonation is ignored in the life cycle analysis of concrete infrastructure, then emissions can be overestimated by 13-48%, depending on the type of cement and the application for recycled aggregates. Carbonation beings at the outer surface and moves progressively inwards, and the depth of carbonation is proportional to the square root of exposure time; it can be described Equation 2.2 (Pade and Guimaraes, 2007) where \(d\) is the depth carbonation (mm), \(k\) is the rate constant (mm/year\(^{0.5}\)), and \(t\) is time (years). Carbonation occurs in the aqueous phase and is controlled by the diffusion of CO\(_2\) or carbonate ions into the concrete (Lagerbald, 2005).

---

\(^9\) Converted from 2.4 L diesel per tonne of sand at 11.1kWh/L diesel
\(^{10}\) Diesel emits 0.27 kg/kWh
\[ d = k \times t^{0.5} \] (2.2)

The rate constant is highly dependent on the exposure conditions, and also on the strength of the concrete. The rate constant of the exposure conditions in Table 2.3 can vary between 0.5 and 15, meaning that after 50 years of service life, the depth of carbonation can range from 3.5 mm to 106 mm. Higher temperatures accelerate carbonation via promoting diffusion, and although the carbonation reaction takes place in the aqueous phase, wet and submerged conditions slow the rate at which carbonation proceeds through the particle. This is because a shell of CaCO\(_3\) forms on the surface of the particle and mitigates the diffusion of CO\(_2\) and carbonate ions into the interior of the particle (Lagerbald, 2005). It should be noted that ready-mixed concrete (used for structural elements) has a compressive strength greater than 15 MPa (Pade and Guimares, 2007), this is important because carbonation kinetics are slower in stronger concrete.

As seen in Table 2.3, “buried” concrete can carbonate, however at a slower rate than exposed concrete. The reason why buried concrete can carbonate is because of CO\(_2\) release from decaying organic matter in soil; a lower degree of compaction in soil also assists the ingress of CO\(_2\) into the soil from above surface (Lagerbald, 2005). The “buried” condition in Table 2.3 might not accurately represent the exposure conditions recycled concrete aggregates would be exposed to if they are either encased in new concrete or compacted and covered by asphalt in road construction.
Table 2.3: The carbonation rate constants (mm/(year)$^{0.5}$) in various conditions with different concrete strengths (Lagerblad, 2005).

<table>
<thead>
<tr>
<th>Exposure Condition</th>
<th>Compressive Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;15 MPa</td>
</tr>
<tr>
<td>Exposed</td>
<td>5</td>
</tr>
<tr>
<td>Sheltered</td>
<td>10</td>
</tr>
<tr>
<td>Indoors</td>
<td>15</td>
</tr>
<tr>
<td>Wet</td>
<td>2</td>
</tr>
<tr>
<td>Buried</td>
<td>3</td>
</tr>
</tbody>
</table>

### 2.2 Leaching and Mineral Carbonation

Several mineral carbonation methods have been proposed by other authors that focus on CO$_2$ capture from thermal power plants. This approach can allow the exhaust gases (~5-15% CO$_2$) to be bubbled through the calcium solution, thereby producing PCC (Kodama et al., 2008). The focus of this thesis, however, is on a method that precipitates CaCO$_3$ via Na$_2$CO$_3$ addition in order to enable CO$_2$ sourcing from the atmosphere (Zeman, 2007). The method of interest also allows for the recovery a pure CaCO$_3$ product (i.e. CaCO$_3$ is precipitated in vessel separate from the residual waste concrete). The following section summarizes the most pertinent concepts and findings from the literature review on mineral carbonation methods; for more detail on other mineral carbonation methods see Appendix A.

### 2.2.1 Mineral Carbonation and Ca/Mg Leaching

The main objective of mineral carbonation is to sequester CO$_2$ in solid form through the production of carbonate minerals (CaCO$_3$ and MgCO$_3$) from calcium and magnesium oxides that are found in naturally occurring silicate minerals and in some industrial waste products (IPCC, 2005). The carbonation of silicate minerals proceeds naturally via weathering, however it proceeds slowly and Lackner et al. (1995) proposed accelerating the process by leaching Ca$^{2+}$/Mg$^{2+}$ with an acid before carbonating them in separate step. In order for the carbonates to precipitate, CO$_2$ must be dissolved into the solution (naturally reducing pH) while the solution...
should be alkaline enough so that the dissolved CO$_2$ dissociates to carbonate ions (CO$_3^{2-}$) and can precipitate as CaCO$_3$ and/or MgCO$_3$.

The use of industrial waste products has received interest over natural silicate minerals (such as serpentine and wollastonite) because of their low cost, and in the case of waste cement, finely ground particles can be obtained as a byproduct from existing practices without additional pulverization (Shuto et al., 2014). An additional advantage of using alkaline industrial wastes instead of natural minerals is that industrial wastes are typically more chemically reactive than naturally occurring minerals (Teir et al. 2007), (Yamasaki et al. 2006) (Abe et al. 2013). The greater reactivity of industrial wastes over natural silicates might be related to a lack of crystal structure, Lea (1970) stated that the hydrated calcium silicates in cement are present as amorphous or nearly amorphous phases (p. 250).

The first step in carbonation is leaching the cations present in the host material. Both natural and anthropogenic silicate minerals can be difficult to dissolve and a SiO$_2$ layer can form on the particles inhibiting efficient Ca/Mg leaching from larger particles (Kakizawa et al., 2001). For this reason, it has been recommended that the particle size should not exceed 500 µm in diameter (Eloneva et al., 2010). Specifically, the authors found that the calcium extraction efficiency decreased from ~55% with the 250-500 µm fraction to ~30% with the 500-1000 µm fraction after 1 hour of leaching steelmaking slag with ammonium nitrate; the extraction efficiency from the 0-125 µm fraction was ~60%.

In addition to forming a shell that inhibits leaching, SiO$_2$ can also be leached from silicates as microscopic particles (Dp<0.45 µm) that are not separated by filtration, forming a colloid (Bao et al., 2010). Some authors have also noted that a silica gel can also form, particularly with longer leaching times, that significantly impedes filtration (Eloneva, 2010).
The choice of acid is an important process decision as stronger acids will naturally extract more (Teir, 2008) but necessitate more energy for recovery. Shuto et al. (2014) studied the leaching of calcium and impurities from “waste cement” by nitric acid; the waste cement was recovered from a waste concrete aggregate recycling facility. The particles used were below 212 µm in diameter and the sample contained ~32% Ca by weight along with significant quantities of Si, Al, and Fe. The authors found that the most important variable for leaching was the ratio between the moles of acid added to the moles calcium in the mass of waste cement being used (N/Ca for nitric acid). A N/Ca ratio of 2.0 means the stoichiometric amount of acid required to dissolve all the calcium was added:

\[3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}(s) + 6\text{HNO}_3(aq) \rightarrow 3\text{Ca(NO}_3)_2(aq) + 2\text{SiO}_2(s) + 6\text{H}_2\text{O}\]  \hspace{1cm} (2.3)

N/Ca values between 0.38 and 7.7 were studied, and approximately 45% of the calcium was leached when the N/Ca was 1.5; the calcium extraction efficiency did not increase significantly when the N/Ca was increased to 7.7 (i.e. with an excess of acid). Calcium leaching was found to occur within the first 10 minutes in every case, and calcium concentrations did not significantly change after two hours of leaching, or even after 24 hours.

Shuto et al. (2014) did observe an increase in pH over two hours of leaching with N/Ca ratios ≤ 0.77, and the increase in pH correlated to the removal of Fe, Al, and Si from solution, but not the increase of calcium. More acidic solutions were produced at higher calcium extraction efficiencies (higher N/Ca), and acidic solutions correlated to high concentrations of impurities (Al, Fe and Si). The authors seemed identify a N/Ca of 0.65 to be the most promising because ~30% of the calcium could be selectively leached. With an extraction efficiency of ~30%, it may be difficult to verify if most of the calcium was leached from \(\text{Ca(OH)}_2\) and possibly some \(\text{CaCO}_3\), rather than the calcium silicate phases.
Nitric acid concentrations between 0.3 M and 3.0 M were tested with N/Ca fixed at 0.65 by Shuto et al. (2014), targeting a recovery of 32.5% of the Ca present. The concentration of the acid was found to have no significant effect on leaching or pH after two hours; however the pH of the solution increased more rapidly at higher concentrations (i.e. impurities were removed more rapidly). Although not explained by the authors, this result might be explained by improved mixing at the higher concentrations because of a lower liquid to solid ratio.

In a subsequent study, Shuto et al. (2015) used acetic acid for leaching and found that ~40% of the calcium could be leached when the acetic acid to calcium molar ratio (AA/Ca) was 2, the pH after two hours of leaching was ~8.0 and the concentration of impurities was not reported.

Bao et al. (2010) studied the influence of mixing speed and temperature on the leaching of metals and silicon from steelmaking slags by acetic acid. Increasing the stirring speed from 300 rpm to 650 rpm did not have a significant effect on Ca/Mg leaching as it increased by a modest ~1%. However, high temperatures (up to 94°C) significantly improved the extraction efficiency of calcium and magnesium, while also resulting in less Fe, Al and Si in solution after an hour of leaching. Although heating solutions appears to be advantageous, it might require a significant amount of energy input. As a simplified estimate, heating one cubic meter of water from 20°C to 94°C requires 86 kWh\(^{11}\), meaning that 3,400 kWh might be required to produce a tonne of CaCO\(_3\) if the solution contained 0.25 M Ca\(^{2+}\), or 340 kWh for 2.5 M Ca\(^{2+}\). This is at least half the energy demand of conventional PCC production.

In addition to heating the solutions (Bao et al., 2010) and selectively leaching calcium at lower extraction efficiencies (Shuto et al., 2014 and Kodama et al., 2008), the levels of impurities can also be controlled via the pH swing method (Park and Fan, 2004). This method can allow for

\(^{11}\) Heat (cal.) = (g of water)(\Delta T°C)(specific heat of water) = (10^6 g)(74°C)(\frac{1 cal}{g°C}) = 74,000 kcal = 86 kWh
both a higher Ca/Mg extraction efficiency with a stronger acid and the production of a potentially marketable carbonate product by precipitating impurities, namely iron, through increasing the pH to ~8.6 between the leaching and carbonation steps.

In most of the reviewed literature, the carbonation/precipitation step has been accomplished by introducing gaseous CO$_2$ into an alkaline Ca/Mg-bearing solution where approximately 80% of the leached calcium was precipitated (Kodama et al., 2008 and Eloneva et al., 2008). Shuto et al. (2014), however, used Na$_2$CO$_3$ to introduce the CO$_2$, where the moles of Na$_2$CO$_3$ added was equal to one-half of the moles of nitric acid used for calcium leaching (i.e. so the moles of Na$_2$CO$_3$ was equal to the expected moles of dissolved calcium). The calcium precipitation efficiency was found to be ~99.4%, although the remaining calcium concentration was 378 mg/L. This is significantly higher than the solubility of CaCO$_3$ under atmospheric conditions (56 mg Ca$^{2+}$/L (White, 2014)); the authors explained this as being due to residual calcium nitrate.

It should be noted that comparing the extraction efficiency of different solvents by comparing the results of various authors is difficult due to unknown differences in the mineralogy and crystallinity of the materials, as well as the leaching conditions (mixing speed, particle size, and solid:liquid ratio, etc.). A side by side comparison of extraction efficiency was found in a doctoral dissertation (Teir, 2008) where consistent materials and methods were used for several solvents. To summarize, the extraction efficiencies of H$_2$SO$_4$ and HCl were ~25%, ~17.5% for HNO$_3$, ~5% for CH$_3$COOH, and ~1% for a variety of ammonium salts after one hour of leaching Mg from finely ground (74–125 µm) serpentine rock, where the moles of acid added was in excess of the magnesium in the solids. In the context of this thesis, these results suggest that significantly higher extraction efficiencies might be obtained from waste cement if HCl is used instead of HNO$_3$, acetic acid, or an ammonium salt.
2.2.2 Calcium Leaching in Deionized Water

The hydration of cement produces Ca(OH)$_2$ and calcium silicate hydrate phases that are both suitable for CO$_2$ sequestration through mineral carbonation. Stolaroff et al. (2005) studied the dissolution of calcium from waste concrete in deionized water. Low P$_{CO_2}$ conditions were used for leaching by introducing N$_2$ to prevent the carbonation of leached calcium by atmospheric CO$_2$; dissolved inorganic carbon levels were not measured. Although not discussed, low P$_{CO_2}$ conditions also likely inhibited the dissolution of calcium from CaCO$_3$ (White, 2013), which may have been sourced from crushed limestone aggregates or carbonated cement. The authors identified Ca(OH)$_2$ and CaCO$_3$ as the only crystalline calcium-bearing phases in the waste concrete by XRD. Some amorphous calcium silicate hydrate (from hydrated cement) was also likely present in the material, and might not be detectable by XRD due to lack of crystal structure. The leaching results were presented in mg of Ca dissolved per gram concrete, while the measured calcium concentrations were not reported. A maximum of ~55 mg of calcium were dissolved per gram of concrete after 10 hours of leaching at 450 rpm. This suggests that the source material contained at least 5.5 wt% calcium (the approximate level of cement calcium in concrete). If one assumed that the composition of the source material was equal to that of bulk waste concrete (Figure 1.1) then the leaching results suggest that 100% of the cement calcium was leached (including from the calcium silicate hydrate). However, this assumption is invalid because depending on how source materials are recovered from waste concrete, they can contain up to 24 wt% uncarbonated cement calcium (Iizuka, 2006).

Gerard et al. (2002) reviewed that the Ca(OH)$_2$ starts to dissolve in deionized water when the calcium concentration in the pore water is diluted to ~20 mmols/L, and that calcium from the calcium silicate hydrate component starts to dissolve when the concentration of calcium is diluted to ~2.0 mmols/L. Efficient leaching of calcium from the calcium silicate hydrate was shown to require further dilution to ~0.5 mmols/L of calcium.
Therefore leaching calcium from the calcium silicate hydrated component with deionized water does not appear to be a promising approach for PCC production with a Na$_2$CO$_3$ based process (the focus of this thesis) because:

1) The leaching of calcium from the silicate components would likely be inhibited by the dissolution of calcium from Ca(OH)$_2$ and also possibly from the dissolution of CaCO$_3$ from crushed limestone aggregate or carbonated cement. Therefore with a method based on CaCO$_3$ precipitation by Na$_2$CO$_3$ addition (the focus of this thesis), several cycles of leaching, precipitation, and deionized water recycling might be needed in order to first dissolve the more soluble calcium phases before the leaching of calcium from the highly insoluble silicates begins.

2) If the calcium concentration in solution is ~0.5 mmols/L after calcium has been efficiently leached from the silicates, then 20,000 L of water would be required to produce 1 kg of CaCO$_3$. If reverse osmosis is used as a desalination technique to recycle deionized water after Na$_2$CO$_3$ addition, then approximately 3.5 kWh/1000 L of water would be required (reviewed in Ismail, 2003); therefore 70,000 kWh would be required per tonne of CaCO$_3$. This also assumes that Ca$^{2+}$ is fully precipitated, however efficiently precipitating calcium from a 0.5 mmol/L solution (equivalent to 0.02 mg/L Ca) might be challenging; Na$_2$CO$_3$ is used in brine treatment remove calcium to below 2 mg/L (Ullmann’s, 1996).

3) The intention of Stolaroff et al. (2005) was to carbonate of portlandite (Ca(OH)$_2$) component alone and not the calcium silicate hydrate (C-S-H), nor did they intend to recover PCC.
2.3 Removing Impurities via pH Swing

Previous authors have shown that achieving a high calcium extraction efficiency from alkaline waste materials resulted in the co-extraction of other elements. In this section, the purification of solutions by alkalinisation is reviewed. The most relevant impurities are iron, manganese, aluminum, magnesium, and silicon; of these iron and manganese are believed to be the most important because they are likely to precipitate and discolour PCC (reviewed in Teir et al. 2005). The solubility of silicates and hydroxides are relevant to this purification section.

2.3.1 Ionic Strength and Activity

Ionic strength and activity are reviewed in detail in Appendix G, along with their influence on the solubility of metals. To summarize, ionic strength can influence the solubility of metals though the formation of aqueous complexes (i.e. by influencing activity, the effective concentration). Ionic strength \( I \) can be calculated from Equation 2.4 in units of molality (moles solute/kg solvent) or molarity (moles/L), and is determined by the ionic concentration \( m \) and by the ion charge \( z \). The ionic strength of a 0.25 M CaCl\(_2\) solution, for example, can be calculated to be 0.75 M.

\[
I = \frac{1}{2} \sum_j m_j z_j^2
\]  

(2.4)

Once the ionic strength is known, activity coefficients can be calculated to determine how ionic strength will influence the solubility of metals. The activity \( \alpha \) of a species is equal to its concentration \( m \) times the activity coefficient \( \gamma \). There are different models to calculate activity coefficients. White (2013) explained that the Davies equation (Equation 2.5) is best suited for calculating activity coefficients in solutions with an ionic strength between 0.1 and 1.0 M.

\[
\log_{10} \gamma_i = -Az_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I} - bI} \right)
\]  

(2.5)
where A is 0.5092 at 25°C and b is approximately 0.3. The Truesdell and Jones model was said to better account for all the effects on activity coefficients at higher ionic strengths, and the Debye-Huckel equation is best suited for low ionic strengths.

Metal solubility increases with increasing ionic strength up to ~0.5 M (i.e. a CaCl₂ concentration of ~0.17 M), and beyond that the solubility of metals starts to slowly decrease for reasons explained in Appendix G. Equation 2.5 calculates that the activity coefficients for divalent ions decreases from ~0.7 to ~0.3 when the ionic strength increases from 0.01 M to 0.5 M, meaning that Ca(OH)₂ solubility, for example, increases by a factor of more than two at any given pH by increasing the ionic strength from 0.01 M to 0.5 M.

2.3.2 Silica

The leaching of microscopic silica particles from calcium silicates, the solubility of silica, and the precipitation of calcium/magnesium silicates (among others) in alkaline conditions are important to the purification step. This is because in acidic conditions, silica can be leached from silicates as microscopic particles that are not removed by filtration. As the pH becomes increasingly alkaline in the purification step, silica particles can dissolve and react with the dissolved calcium to re-precipitate as calcium silicates. Silicate precipitation is more difficult to predict than hydroxide precipitation, as it is also dependent on the activity of dissolved silica and several different silicate phases can precipitate. Most importantly, dissolved metals can precipitate as silicates in significantly less alkaline solutions than the hydroxide of the same metal, and silicates also precipitate sooner with higher activities of dissolved silica (White, 2013).

2.3.2.1 Silicic Colloids and Waste Cement Leaching

Silicon is a major component of concrete and cement, as it is found in quartz sand (fine aggregate) and in calcium silicates (cement). Previous authors (Shuto et al., 2014) found that when using nitric acid up to 30% of the silicon in waste cement was leached when approximately
45% of the calcium was leached from waste cement (with a Ca:Si molar ratio of approximately 2:1 in the filtered solution after leaching). A minimal amount of Si was leached after two hours at lower calcium extraction efficiencies. The leaching of silicon from calcium silicates in acidic solutions has been explained to form a silicic colloid (Bao et al., 2010). The microscopic (<0.45 μm) SiO₂ particles are not readily removed by filtration or sedimentation.

2.3.2.2 The Solubility of Silica

The solubility of silica (SiO₂) is important because the activity of dissolved silica influences the solubility of silicates, and therefore is relevant to the re-precipitation of calcium as calcium silicates in the purification step because microscopic silica particles can be leached which are not removed by filtration. Silica solubility is typically described by as the formation of silicic acid (H₄SiO₄) from quartz (crystalline silica) and/or amorphous silica, where amorphous silica is 20 times more soluble than quartz at any given pH (White, 2013):

\[
\text{SiO}_2(\text{qtz}) + 2\text{H}_2\text{O} \leftrightarrow \text{H}_4\text{SiO}_4(\text{aq}) \quad K_{\text{qtz}} = 10^{-4} \quad (2.6)
\]

\[
\text{SiO}_2(\text{amorphous}) + 2\text{H}_2\text{O} \leftrightarrow \text{H}_4\text{SiO}_4(\text{aq}) \quad K_{\text{qtz}} = 2 \times 10^{-3} \quad (2.7)
\]

Similar to carbonic acid, silicic acid also dissociates as pH increases:

\[
\text{H}_4\text{SiO}_4 \leftrightarrow \text{H}_3\text{SiO}_4^- + \text{H}^+ \quad (2.8)
\]

\[
K_1 = \frac{\alpha_{\text{H}_3\text{SiO}_4^-} \alpha_{\text{H}^+}}{\alpha_{\text{H}_4\text{SiO}_4}} = 10^{-9.9} \quad (2.9)
\]

and

\[
\text{H}_3\text{SiO}_4^- \leftrightarrow \text{H}_2\text{SiO}_3^{2-} + \text{H}^+ \quad (2.10)
\]

\[
K_2 = \frac{\alpha_{\text{H}_2\text{SiO}_3^{2-}} \alpha_{\text{H}^+}}{\alpha_{\text{H}_3\text{SiO}_4^-}} = 10^{11.7} \quad (2.11)
\]

The second dissociation reaction can also be defined as:
\[ H_4SiO_4 \leftrightarrow H_2SiO_4^{2-} + 2H^+ \]  
\[ K_2^* = \frac{\alpha_{H_2SiO_4^{2-}}}{\alpha_{H_4SiO_4}} \alpha_{H_2^+}^2 = 10^{9.9} \times 10^{-11.7} = 10^{-21.6} \]  

The total concentration of dissolved silica (i.e. the sum of \( H_4SiO_4 \), \( H_3SiO_4^- \), and \( H_2SiO_4^{2-} \)) as a function of pH can then be represented by the following equation (White, 2013):

\[ [SiO_2]_T = [H_4SiO_4] \left[ 1 + \frac{K_1}{[H^+]^2} + \frac{K_1 K_2}{[H^+]^3} \right] \]  

The ionic silica species (\( H_3SiO_4^- \) and \( H_2SiO_4^{2-} \)) are of particular interest because they can react with dissolved metals such as \( Al^{3+}, Mg^{2+}, \) and \( Ca^{2+} \) to form insoluble silicate minerals. From Figure 2.2 it can be seen that the concentration of the ionic silica species increase as pH increases, while the concentration of \( H_4SiO_4 \) remains constant. This suggests purification be limited to less than approximately pH 9.5 to avoid excessive formation of ionic silica.

![Figure 2.2: The activity of dissolved silica in equilibrium with quartz and amorphous silica vs. pH (reproduced from White, 2013 with modifications). Assumes no dissolved aluminum, calcium, or magnesium etc.](image)

2.3.2.3 Silicate Solubility

In solutions containing dissolved silica, the solubility of a metal vs. pH can be controlled by silicate precipitation, rather than hydroxide precipitation. The solubility of silicates is
generally described by incongruent dissolution, where the mineral does not dissolve in the conventional sense, but reacts with water to form new minerals in place of the original while releasing some ions into solution. For example, the solubility of kaolinite (Al₂SiO₅(OH)₄) was described by White (2013) as:

\[
\frac{1}{2} \text{Al}_2\text{SiO}_5(\text{OH})_4(s) + \frac{5}{2} \text{H}_2\text{O} \leftrightarrow \text{Al}((\text{OH})_3(s) + \text{H}_4\text{SiO}_4
\]

(2.15)

\[K = \alpha_{\text{H}_4\text{SiO}_4} = 10^{-4.4}
\]

(2.16)

meaning that with H₄SiO₄ activities greater than 10⁻⁴.⁴, the aluminum silicate (kaolinite) is more stable (i.e. less soluble) than aluminum hydroxide, and will precipitate before the hydroxide. The relative solubility of aluminum hydroxide (gibbsite) compared to aluminum silicates (kaolinite and pyrophyllite) as a function of pH at different dissolved silica activities was shown in White (2013), where only at the lowest dissolved silica activities does aluminum hydroxide precipitate before one of the aluminum silicates. The solubility of all three aluminum species starts to rebound in alkaline solutions because Al³⁺ becomes increasingly hydrolyzed and Al(OH)₄⁻ complexes form; this is typical of highly charged (≥3⁺) metal ions.

### 2.3.3 Hydroxide Solubility in a Calcium-Rich Solution

The solubility of hydroxides is relevant to the purification step because if essentially no silica is present, then the solubility of metals will likely be controlled by hydroxide precipitation as pH increases (White, 2013). Figure 2.6 represents the solubility of various hydroxides as a function of pH in a 0.25 M CaCl₂ solution. The figure was constructed through calculations included in Appendix H. The ionic strength was calculated to be 0.75 M, and activity coefficients (\(\gamma\)) were calculated to be 0.326 for divalent cations, and 0.0802 for trivalent cations with Davies Equation (Equation 2.5).
Figure 2.3: The solubility of various metal hydroxides in 0.25 M CaCl₂ solution (ionic strength = 0.75 M) vs. pH. Reproduced from White (2013) with modifications.

From Figure 2.3 it can be seen that calcium hydroxide is the most soluble of the hydroxides listed, even with the influence of the common ion effect from 0.25 M CaCl₂ (for review of the common ion effect see Appendix H). This could mean that calcium is first to start leaching as the pH decreases, and also that calcium is the last to start precipitating as pH increases. The Ca(OH)₂ curve represents how much Ca(OH)₂ can exist in a 0.25 M CaCl₂ solution vs. pH. Once the pH exceeds 11.9 (e.g. by the addition of NaOH), the solution is interpreted to become supersaturated with respect to Ca(OH)₂. As the pH continues to exceed 11.9 the total calcium concentration continues to decrease, the curve is asymptotic because beyond pH 11.9, the CaCl₂ is no longer 0.25 M. It can also be seen that the solubility of iron in neutral waters is dramatically reduced when ferrous iron is oxidized to ferric iron. If the solutions are sufficiently free of silica, then the fraction of calcium in solution relative to other metals could be predicted via hydroxide solubility calculations (Appendix I).
2.3.4 Acidity

In addition to $H^+$, metals also contribute to acidity by acting as a pH buffer when alkalinity is added. Hughes and Grey (2013) explained that acidity can be calculated according to the follow equation, where the effective acidity ($A_{eff}$) is reported as mg/L as CaCO$_3$:

$$A_{eff} = 50 \times \left(1000 \times (10^{-pH}) + \frac{2(Fe^{2+}) + 3(Fe^{3+})}{56} + \frac{2(Mn)}{55} + \frac{3(Al)}{27} + \frac{2(Zn)}{65}\right) \quad (2.17)$$

This suggests that the amount of alkalinity required to reach a given pH during the purification step may not be accurately predicted by only measuring the initial pH.

2.3.5 Sulphate-Sulphide System

With respect to this thesis, the speciation of sulphur is relevant to the outgasing of $H_2S$ and to the incorporation of barium into the PCC (BaSO$_4$ is highly insoluble). Dissolved sulphur can be present in solution as different species depending on pH and the redox conditions. The dissociation of H$_2$SO$_4$ to HSO$_4^-$ and SO$_4^{2-}$ is applicable to oxidizing conditions, and the dissociation of H$_2$S (a slightly soluble acid gas) to HS$^-$ and S$^2-$ is applicable to reducing conditions; pKa values represent the pH at which the dissociation is 50% complete, and $pK_a = -\log(K)$. These pKa values become vertical lines in Figure 2.7, which was constructed as described in Appendix L. The upper and lower limits are defined by the stability of water in the standard state (White, 2013), while the transition of sulphate to sulphide species is defined in Appendix J.

$$H_2SO_4 \leftrightarrow HSO_4^- + H^+ \quad pK_{a1} = -1.98 \quad (2.18)$$

$$HSO_4^- \leftrightarrow SO_4^{2-} + H^+ \quad pK_{a2} = 1.98 \quad (2.19)$$

$$H_2S \leftrightarrow HS^- + H^+ \quad pK_{a1} = 7 \quad (2.20)$$

$$HS^- \leftrightarrow S^{2-} + H^+ \quad pK_{a2} = 12.9 \quad (2.21)$$
Figure 2.4: Predominance regions for dissolved sulphur species, constructed with $\Delta G^o_f$ values from White (2013) at 25°C and 0.1 MPa.

Before the chemical regeneration step, sulphate levels in the feed solution should be below 5 g/L (0.052 M) to avoid the corrosion of steel cathodes (where reduction occurs) in membrane electrolysis units (Ullmann’s, 1996 and IPPC, 2001). The solubility of sulphate will likely be controlled by the solubility of gypsum in this process, which would be suppressed by the common ion effect of CaCl$_2$ (Li and Demopoulos, 2005). The authors calculated the solubility of gypsum in a 0.25 mol/kg CaCl$_2$ solution at 295 K (similar to these experiments) to be ~0.008 mol/kg, compared to ~0.015 mol/kg without CaCl$_2$.

2.4 Carbon Capture and Sodium Carbonate Production

In order to produce CaCO$_3$, a source of CO$_3^{2-}$ is required, in this thesis Na$_2$CO$_3$ is used to as the source. The absorption of CO$_2$, an acid gas, by alkaline solutions is reviewed in the following section.

2.4.1 Stationary Sources

Carbon capture and storage (CCS) from stationary sources typically involves producing a pure stream of CO$_2$ from the flue gases of thermal power plants. High purity streams of CO$_2$ can
then be transported via pipeline to disposal sites for 1-8 $US/t CO_2 per 250 km (IPCC, 2005).

The first step in this process is to absorb CO_2 from the flue gas.

One of the well-established methods involves the absorption of CO_2 by NaOH and Na_2CO_3 solutions (Hikita et al., 1976).

$$2NaOH_{(aq)} + CO_2_{(g)} \rightarrow Na_2CO_3_{(aq)} + H_2O \quad \Delta H = -108.8 \text{ kJ/mol} \quad (2.22)$$

$$Na_2CO_3_{(aq)} + CO_2_{(g)} + H_2O \rightarrow 2NaHCO_3_{(aq)} \quad \Delta H = -26.6 \text{ kJ/mol} \quad (2.23)$$

Where NaHCO_3 is produced, a stream of pure CO_2 is recovered by heating the solution (reviewed in Floyd et al., 2013). The Na_2CO_3 solution can be used to precipitate CaCO_3 if it is mixed with a calcium-rich solution (Shuto et al., 2014).

Ammonia is also used to absorb CO_2, as is done in Solvay process, where Na_2CO_3 is produced on an industrial scale (Gao et al., 2007). A method that resembles a modified Solvay process was proposed to sequester CO_2 through the production of CaCO_3 from CaO-rich industrial wastes (Kodama et al. 2008). The authors estimated that with a gas stream containing 13% CO_2 and 87% N_2, the process would require ~130 kWh per ton of CaCO_3, where more than half the energy consumption was from pulverizing the industrial waste (steelmaking slag); the 80% passing size of the crushed slag was 440 µm, and the work index was 30.4 kWh/t slag (almost double that of granite). The volatilization of ammonia gas during the CO_2 absorption step was thought to be problematic, however, Eloneva et al. (2012) concluded the process still had economic potential despite these losses. Kodama et al. (2008) proposed that ammonia emissions could be mitigated if the ammonia-rich gas steam was bubbled though sulphuric acid, thus producing ammonium sulfate (commonly used as soil fertilizer) as a byproduct.

2.4.2 Air Capture

The main role of air capture is to offset the emissions from small and mobile CO_2 sources such as transportation vehicles while utilizing renewable energy sources; air capture has been investigated by several authors (Baciocchi et al., 2006; Keith et al., 2006; Zeman, 2007 and
Mahmoudkhani et al., 2009). Carbonate solutions are not used in air capture methods because they have an exceedingly slow adsorption rate due to the relatively low partial pressure of CO₂ in air compared to flue gas, therefore hydroxide solutions have been used instead to obtain a more acceptable absorption rate.

The end product of air capture is therefore sodium carbonate (or potassium carbonate if potassium hydroxide was used); the significance of this is that sodium carbonate does not release its adsorbed CO₂ as easily as sodium bicarbonate, and hence more energy intensive methods are required to recover the CO₂ for storage. One such method includes a causticization step, which was studied by Zeman (2007). In this method calcium hydroxide is added to the sodium carbonate solution to precipitate the absorbed CO₂ as calcium carbonate, and regenerate the sodium hydroxide. Although CO₂ is safely stored as calcium carbonate, calcium hydroxide needs to be regenerated, so the calcium carbonate is thermally decomposed at 900°C to produce calcium oxide and a pure gas stream of CO₂. The CO₂ can then be compressed and stored, and the calcium oxide is added to water to reproduce calcium hydroxide.

The design of Zeman (2007) was said to provide sufficient surface area contact between a 1M sodium hydroxide solution and air to achieve a 50% capture rate with an inlet concentration of 380ppm CO₂. These air capture systems required a significant amount of energy to power the air blowers: 528 kWh/tonne CO₂ in the Zeman (2014) process, and 189 kWh/tonne CO₂ in the Baciocchi et al. (2006) process; the difference between these two results was likely because Baciocchi et al. (2006) used a gas stream containing 500 ppm CO₂.

In other work, Mahmoudkhani et al. (2009) experimentally determined that CO₂ could be absorbed by sodium hydroxide for 150 kWh/tonne CO₂, this value included the energy demand

---

12 Converted from 479 kWh/ton
13 Converted from 30kJ/mol CO₂
14 Converted from 136 kWh/ton CO₂
for both the air driver (fan) and for the fluid pump. The conditions were such that the air speed was set at 0.7 m/s and fluid flow at 3.6 L/m²·s through the packing; a 3M NaOH solution was used and the CO₂ concentration across the adsorption tower decreased by 68%. It should be noted that the product of air capture is not a pure Na₂CO₃ solution, but a mixture of NaOH and Na₂CO₃. Once the Na₂CO₃ is used to precipitate CaCO₃, NaOH will need to be regenerated for the next CO₂ absorption cycle (except in the causticization method, where NaOH is regenerated when Na₂CO₃ reacts with Ca(OH)₂ to precipitate CaCO₃).

2.5 Reagent Recycling

The process of interest combines Na₂CO₃ with CaCl₂ to produce PCC and a salt (NaCl) solution. In a once through design, the process would require the purchase of Na₂CO₃ and HCl as well as the disposal of NaCl solution. This will likely lead to cost overruns and fugitive CO₂ emissions thus negating the sustainability objectives. A regent recycling method is therefore needed to prevent the production of waste. Two methods are investigated.

2.5.1 Membrane Electrolysis

One process for regenerating HCl and NaOH is membrane electrolysis (i.e. the chlor-alkali process). This process typically produces chlorine gas (Cl₂), hydrogen gas (H₂) and aqueous NaOH (Equation 2.24) from a ~5.3 M sodium chloride brine (IPPC, 2001). Hydrogen chloride gas can be produced by reacting the chlorine and hydrogen gases in a separate reactor. The reaction (Equation 2.25) is exothermic and is typically done in an installation called an HCl oven (Teir et al., 2009). Hydrochloric acid can then be made through the dissolution of hydrogen chloride gas in water.

\[
\text{NaCl(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{NaOH(aq)} + \frac{1}{2} \text{Cl}_2(g) + \frac{1}{2} \text{H}_2(g) \quad \Delta H = -223 \text{ kJ/mol NaOH} \quad (2.24)
\]

\[
\text{Cl}_2(g) + \text{H}_2(g) \rightarrow 2\text{HCl(g)} \quad \Delta H = -176 \text{ kJ/mol NaOH} \quad (2.25)
\]
Figure 2.5: Simplified process scheme for membrane electrolysis (modified from IPPC, 2001). Cl$_2$ is produced at the anode through the oxidation of Cl$^-$ sourced from NaCl. The electric field induces the migration of positive ions across a membrane into the cathode chamber where H$_2$ and NaOH are produced through the reduction of water and influx of Na$^+$. Some authors have proposed the use of membrane electrolysis for carbon sequestration applications (House et al., 2009). This method requires 2,350 kWh to produce a tonne of NaOH (reviewed in Koter and Warszawski, 2000), and therefore 1,880 kWh/tonne CaCO$_3$\textsuperscript{15}.

Once the brine has been depleted to 2.6-4.3 M NaCl, it is re-saturated and treated to remove calcium, magnesium, iron and sulphate ions. If the brine contains significant levels calcium or magnesium, the formation of NaOH will cause the precipitation of calcium and magnesium hydroxide, which would rapidly foul the membrane. Iron discolours the caustic liquor, and sulphate causes the corrosion of the steel cathode cell (IPPC, 2001). For membrane electrolysis, the brine should ideally contain less than 2 mg/L of calcium, less than 1 mg/L of magnesium, and less than 5 g/L sulphate after primary purification (Ullmann’s, 1996). Any bicarbonates present in the brine will be decomposed by the acidic conditions, outgassing carbon dioxide.

\textsuperscript{15} Two moles of NaOH used to capture one mole of CO$_2$ precipitating one mole of CaCO$_3$ or 1 tonne NaOH leading to 1.25 tonne CaCO$_3$. 

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2.5.2 Bipolar Membrane Electrodialysis

An alternative to the chlor-alkali process is bipolar membrane electrodialysis (BMED), which can be used to produce equimolar quantities of HCl and NaOH from NaCl. Bipolar membranes (BPM) are composed of a cation exchange membrane (CEM) and an anion exchange membrane (AEM), and can be used to separate H\(^+\) and OH\(^-\) once produced by dissociating water with an electric field. If the electric field directs H\(^+\) into a chamber containing Cl\(^-\), HCl is produced, and if OH\(^-\) are directed into a chamber containing Na\(^+\), NaOH is produced.

\[ \text{NaCl(aq)} + \text{H}_2\text{O} \rightarrow \{\text{NaOH(aq)}\} + \{\text{HCl(aq)}\} \quad \Delta H = 55.6 \text{ kJ/mol NaOH} \quad (2.26) \]

Several membrane configurations can be used to accomplish this (Shuto et al., 2015 and Mazrou et al., 1998), as shown in the following figure.

Figure 2.6: Two configurations for HCl and NaOH regeneration from NaCl through bipolar membrane electrodialysis. Modified from (a) Shuto et al. (2015) and (b) Mazrou et al. (1998).

BMED has several advantages over membrane electrolysis: no toxic and corrosive chlorine gas is generated, lower energy requirements, and the capital and operating costs are approximately half that of the membrane electrolysis method (Nagasubramanian, 1977).

One of the keys to maximizing the energy efficiency of BMED appears to be in producing HCl and NaOH at lower concentrations. Carmen (1993) explained that the loss in efficiency at
higher concentrations is mainly due to increasing leakage of H\(^+\) and OH\(^-\) through the monopolar membranes into the NaCl streams. Specifically, the author found that the current efficiency was ~85\% for 1 M product, and decreased to ~60\% for 2.5 M product; a lower current efficiency represents more leakage of H\(^+\) and OH\(^-\) which lowers the energy efficiency of chemical regeneration. This was also demonstrated by Shuto et al. (2015), who found that the energy consumption for chemical regeneration from NaCl increased with increasing recovery yield, and therefore product concentration. From Shuto and colleagues (2015) it appears the chemicals were be regenerated for ~375 kJ/mol NaOH with a 55\% NaCl recovery, or for ~250 kJ/mole with a 25\% NaCl recovery from a 2.5 M NaCl solution. This is equivalent to 2,604 – 1,736 kWh per tonne of NaOH, or 2,080 - 1,390 kWh per tonne CaCO\(_3\). Lower initial salt concentrations increase recovery yield (Shuto et al., 2014).

The temperature of the NaCl solution also influences energy efficiency. Carmen (1993) demonstrated that a 1 M product could be made from a saturated NaCl brine while consuming 1,700 kWh/tonne NaOH produced\(^\text{16}\) at 30\(^\circ\)C, and 1,565 kWh/tonne NaOH produced\(^\text{17}\) at 40 \(^\circ\)C. The maximum operating temperature recommended was 40\(^\circ\)C; higher temperatures reduce power consumption but can also shorten the membrane life.

Other operating parameters such as voltage and current were studied by Shuto et al. (2014), where they concluded that high voltage (12.5 V) and current (6.0 A) help to increase energy efficiency. The follow up study by Shuto et al. (2015) also explained that the number of cells and membrane configuration also influence energy efficiency.

In Table 2.2, a carbon intensity of 0.04 kg CO\(_2\) per kWh for electricity is used because this value was listed as the carbon intensity for power generation in Ontario in 2015 (CEI, 2015). Also of note is that the thermodynamic minimum for BMED is 80 kJ/mol NaOH (or 160 kJ/mol

\(^{16}\) Converted from short tons to metric tonnes  
\(^{17}\) Converted from short tons to metric tonnes
CO₂-captured) based on the dissociation energy of water in the bipolar membrane (Shuto et al., 2014), this translates to 444.4 kWh/t CaCO₃. Therefore PCC production with a BMED method might become competitive with the conventional method involving limestone calcination on the basis of energy consumption if a high efficiency is achieved.

Table 2.2: Summary of various technologies. Values in bold are in reference to per metric tonne of CaCO₃ produced.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Membrane Electrolysis</th>
<th>Bipolar Membrane Electrodialysis (BMED)</th>
<th>Conventional PCC Production</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl Brine</td>
<td>NaCl Brine¹⁸ 2.5 M NaCl¹⁹</td>
<td>Limestone</td>
</tr>
<tr>
<td>kWh</td>
<td>1,800</td>
<td>1,360</td>
<td>623 (thermal)²</td>
</tr>
<tr>
<td>kg CO₂ Emitted</td>
<td>75.2</td>
<td>54.4</td>
<td>55.6</td>
</tr>
<tr>
<td>CO₂ Balance⁻²⁰</td>
<td>-364.8</td>
<td>-385.6</td>
<td>-384.4</td>
</tr>
<tr>
<td>kg CO₂</td>
<td></td>
<td></td>
<td>210”</td>
</tr>
<tr>
<td>ΔG</td>
<td>208 kJ/mol NaOH</td>
<td>80 kJ/mol NaOH</td>
<td>130 kJ/mol CaO</td>
</tr>
<tr>
<td>ΔH</td>
<td>223 kJ/mol NaOH</td>
<td>55.6 kJ/mol NaOH</td>
<td>178.3 kJ/mol CaO</td>
</tr>
</tbody>
</table>

2.6 Precipitated Calcium Carbonate Production and Product Quality

In the following section the current PCC production methods are reviewed, as well as the properties of PCC that are important for application as a mineral filler in paper manufacturing. Methods to control the properties of the PCC are also reviewed.

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¹⁸ With a 1 M product
¹⁹ At a 25% recovery ratio of NaCl
²⁰ If an ideal 440 kg CO₂ sequestered per tonne CaCO₃ produced via mineral carbonation (all uncarbonated calcium in feedstock material) and carbon intensity of electricity is 0.04 kg CO₂/kWh.
2.6.1 Production Methods

Casey (1983) listed three production methods used for making PCC for paper coating from limestone. All three methods involve the calcination of limestone and then mixing the lime with water to create a slurry. The purity, activity, particle size, concentration, and temperature of the calcium hydroxide suspension, known as “milk of lime,” all have a significant effect on the properties of the end product. The three methods were termed the carbonation, lime-soda and calcium chloride processes.

The carbonation process involves bubbling of the CO$_2$-rich kiln flue gases through the Ca(OH)$_2$ slurry. In this process the main focus is on controlling the properties of the product. The particle shape and size can be controlled by reaction conditions including ion concentration, starting temperature, temperature profile, type and degree of agitation, pH, solution rates, and the addition of auxiliary materials to alter the dimensions and performance characteristics of the PCC. It was said to be the most widely used because it used the most readily available and lowest cost raw materials (Casey, 1983). Oates (1998) stated that the calcium hydroxide slurry is screened to remove coarse particles before carbonation, and that scalenohedral calcite particles are produced by this process when crystallization occurs on the surface of the calcium hydroxide particles.

The lime-soda process involves a reaction between sodium carbonate and the milk of lime, where calcium carbonate and sodium hydroxide are produced:

$$\text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaOH} \quad (2.27)$$

The physical properties of the PCC product are determined by the reaction conditions in this process as well. This process was used by alkali manufactures, where the main objective was to produce caustic soda, and a coarse calcium carbonate was precipitated in order to allow caustic recovery from the pigment cake. A fine PCC can be produced through this process, but not without some trade-offs between efficiency of caustic soda recovery. The same chemical reaction
is used in the Kraft recovery process in converting green liquor into white liquor, and some mills have used the PCC product for paper coating (although most often, the PCC is calcined and reused in the Kraft process). If it is being used for paper coating, the PCC must be treated for alkali content by treatment with CO₂, acids or salts and bleaching may also be required to improve the products colour. Sometimes the PCC has to be ground to reduce its particle size; the energy requirements for this step can be estimated with Bond’s equation, where approximately 35 kWh/tonne PCC might be required to reduce 80% of 6 µm particles to 2 µm particles, for example

The calcium chloride process is where calcium hydroxide is dissolved by ammonium chloride, creating ammonia gas and a calcium chloride solution (reviewed in Teir et al., 2005). The calcium chloride solution is then reacted with a sodium carbonate solution to form the PCC. The reactions are:

\[
\text{Ca(OH)}_2 + 2\text{NH}_4\text{Cl} \rightarrow \text{CaCl}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O} \quad (2.28)
\]

\[
\text{Na}_2\text{CO}_3 + \text{CaCl}_2 \rightarrow \text{CaCO}_3 + 2\text{NaCl} \quad (2.29)
\]

This process can be controlled by addition times, the rate and method of agitation, concentrations, pH, and reaction temperatures. Commercial PCC plants using this process are typically sited near Solvay plants, as they produce CaCl₂ as a waste product of Na₂CO₃ manufacturing (Eloneva, 2010). The Solvay process uses ammonia as a CO₂ sorbent, and the precipitation of PCC from Solvay plant waste products have also been described as (Gao et al., 2007):

\[
(\text{NH}_4)_2\text{CO}_3 + \text{CaCl}_2 \rightarrow \text{CaCO}_3 + 2\text{NH}_4\text{Cl} \quad (2.30)
\]

The production of PCC by this method was terminated in the U.S. in 1975, likely because Solvay plants were replaced by mining trona as the primary source of Na₂CO₃ in the U.S.

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21 Using Wi = 11.7 for limestone
2.6.2 Precipitate Properties

To determine if a batch of mineral filler is suitable for a particular application, the properties that are typically measured for are: particle size, surface area, brightness, and mineralogy; for PCC it is also important to have an SEM image so that the particle shape (morphology) can be identified (Gaudreau, 2015). A chemical analysis of the PCC is not commonly included in the evaluation, possibly because it is used a filler and not a chemical reagent; however the purity (wt% CaCO\textsubscript{3}) is typically over 98% for PCC, and 96% for GCC (reviewed in Casey, 1983).

In paper manufacturing, PCC is used as a filler to improve the products whiteness and opacity, as well as to replace some of more expensive cellulose (Eloneva, 2010). For such applications, 70% of the particles should be below 2µm in diameter, and the ISO brightness should be greater than 93% relative to BaSO\textsubscript{4} (Teir et al., 2005). PCC is also used as a paper coating to improve printability by providing a smooth and ink receptive surface (Eloneva, 2010). When used as a paper coating, the particles should be 0.4-2.0 µm in diameter, and have an ISO brightness greater than 95% (Teir et al., 2005). PCC is mostly used as a filler, and when used as a coating it is usually mixed with clay forming a mixture that is composed of 5-50% calcium carbonate (Eloneva, 2010 and Casey, 1983). For coating-grade calcium carbonate, the prime requisites are: true white colour, no detrimental impurities, non-abrasiveness, and the size and shape of the particles. It has been observed that the absence of coarse particles is more important than the presence of fine particles when it comes to determining the gloss of paper coatings (Casey, 1983); a definition of “coarse particles” was not given but is assumed to refer to those that stand out from the bulk of the particles. The CaCO\textsubscript{3} content of common printer paper is typically between 15-20% wt. (Ricoh, 2015), while high-quality printing papers can have a mineral filler content up to 40% wt. (reviewed in de Alda, 2008).
2.6.3 Purity

The purity of commercial coating-grade PCC is typically above 98% CaCO$_3$ (Casey, 1983 and Roskill, 2012); and almost all PCC is produced by reacting hydrated lime with carbon dioxide (the conventional carbonation process). The most important impurities are iron and manganese as they strongly discolor the product (Teir et al., 2005). For paper making applications, the iron content (expressed as Fe$_2$O$_3$) should be below the limit of 0.1% (Knez et al., 2006). Oates (1998) reviewed that in the conventional PCC production process, it is important to have low levels of MgO, SiO$_2$ and Al$_2$O$_3$ in the lime before the carbonation step because they become incorporated as oversized particles in the PCC. Ground calcium carbonate GCC is also used in paper manufacturing for both coating and filler (reviewed in Teir et al., 2005) and typically contains ~2.4% MgCO$_3$ (Casey, 1993).

MgCO$_3$ (magnesite) is also used as a paper filler because it is also bright, chemically inert and relatively soft. The Mohs scale hardness of magnesite ranges from 3.5-4.5, while the hardness of calcite is 3. This means that magnesite could contribute to premature wearing of machinery (Teir et al., 2005). Magnesite also has a tendency to yellow over time, and since other filler materials are more abundant the investments required for modifying processes and machinery to get a suitable MgCO$_3$ filler material are typically not considered worthwhile (Teir et al., 2005). Some authors (Zhao et al. 2005) have advocated for the use of MgCO$_3$ in papermaking if it was produced through mineral carbonation.
Table 2.3: The Typical Chemical Properties of Calcium Carbonate Pigments (Reviewed in Casey, 1983).

<table>
<thead>
<tr>
<th></th>
<th>GCC</th>
<th>Carbonation</th>
<th>Lime-Soda</th>
<th>Calcium Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃%</td>
<td>96.63</td>
<td>98.36</td>
<td>98.43</td>
<td>98.62</td>
</tr>
<tr>
<td>CaSO₄%</td>
<td>N/A</td>
<td>0.08</td>
<td>0.78</td>
<td>0.63</td>
</tr>
<tr>
<td>MgCO₃%</td>
<td>2.43</td>
<td>0.70</td>
<td>0.37</td>
<td>0.21</td>
</tr>
<tr>
<td>Al₂O₃%</td>
<td>0.28</td>
<td>0.09</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe₂O₃%</td>
<td>0.09</td>
<td>0.07</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>SiO₂%</td>
<td>0.37</td>
<td>0.10</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>NaCl%</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.10</td>
</tr>
<tr>
<td>%H₂O loss at 110ºC</td>
<td>0.20</td>
<td>0.60</td>
<td>0.25</td>
<td>0.30</td>
</tr>
<tr>
<td>pH of a saturated solution</td>
<td>9.1</td>
<td>9.4</td>
<td>10.3</td>
<td>8.5</td>
</tr>
</tbody>
</table>

The barium content of PCC is sometimes listed in the material analysis done by a distributor, and the limit for the barium content in PCC was stated to be 20ppm (Caltron-Clays, 2015). The content of this element in PCC is likely constrained because BaCO₃ is toxic and is often used as rodenticide. Some authors have considered adding BaCO₃ to clinker to inhibit sulphate attack in cement (Carmona-Quiroga and Blanco-Varela, 2015), and the average Ba content of Portland cement is 280 mg/kg (Lea, 1998).

2.6.4 Morphology and Crystal Shape

In addition to purity, brightness, abrasiveness and particle size, the crystal shape is also an important characteristic of precipitated calcium carbonate. Five different forms of PCC were described by Oates (1998): scalenohedral calcite, rhombohedral calcite, amorphous calcium carbonate, aragonite and vaterite. In addition to these, other calcite shapes are produced by commercial PCC manufacturers.

1) The scalenohedral form of calcite is required for most applications. It has a high surface area for a given particle size, and is produced by the carbonation method where crystallization occurs on the surface of calcium hydroxide particles. Carmona et al. (2003) related the morphological
transition of rhombohedral calcite to scalenohedral calcite in the Ca(OH)$_2$-CO$_2$-H$_2$O system to the excess of calcium over carbonate species in solution; conductivity, in units of milli Sieverts per cm (mS/cm) was measured as a proxy for calcium concentration.

2) The rhombohedral form of calcite is usually obtained in precipitation processes by using solution routes, and is rarely produced by the carbonation method. Rhombohedral calcite is primarily used as a coating material, but is also used as a paper filler.

3) Oates (1998) stated that amorphous calcium carbonate (ACC) does not have any industrial applications (likely because it transforms into other more stable morphologies over time) but can be produced by the carbonation method when process control is lost. ACC is the least stable of all the CaCO$_3$ polymorphs, is a monohydrate (Goodwin et al. 2010), and can be precipitated when mixing two supersaturated solutions of CaCl$_2$ and Na$_2$CO$_3$. ACC has been described as the first polymorph to precipitate following Ostwald’s step rule, which states that the least stable polymorph will be the first to precipitate (reviewed in Van Santen, 1984). Although first to precipitate, Rodriguez-Blanco et al. (2011) found that ACC rapidly dehydrates and crystalizes to form individual vaterite particles, which can then transform to calcite via a dissolution and re-precipitation mechanism. The ACC-vaterite transformation was found to be 10 times faster than the vaterite-calcite transformation. Loste et al. (2003) demonstrated that the incorporation of magnesium into ACC increases its stability, and that this effect increases with the molar percentage of magnesium in the ACC. A Mg:Ca molar ratio of 2:1 in solution yielded ACC containing 8 mol% Mg which remained stable for less than 30 minutes, while 24 mol% Mg ACC was produced from a 10:1 Mg:Ca solution and was stable for up to 14 hours. Kellermeier et al. (2013) conducted CaCO$_3$ precipitation experiments at various temperatures and silica concentrations to study their influence on polymorphic transformations. The authors found that silica induced “remarkable changes” in the evolution of polymorphic (C-calcite, V-vaterite, A-aragonite, ACC-amorphous) fractions over time.
4) Oates (1998) stated that vaterite is unstable therefore does not have any industrial applications, however Mori et al. (2010) studied the production and application of vaterite for ink jet paper coating. The authors found that vaterite-coated ink jet paper resulted in a higher print quality than calcite coated paper, and was equal in quality to commercial silica-coated ink jet paper. Silica is generally used as a coating for ink jet paper because it absorbs ink faster than calcite, but it also has a higher production cost. The high quality of vaterite-coated paper was explained by the high hydrophilicity of vaterite, which promoted quick inward absorption of inks before they could spread laterally on the surface of the ink jet paper. Although vaterite was found to quickly absorb ink, crystal transformation can occur and particle diameter can change in aqueous dispersions when they are prepared for paper coating; this transformation may impair printing quality. The temperature of pigment dispersion solutions during coating was said to often be close to 40ºC, which can further impair vaterite stability. After studying the stability of vaterite in various solutions, Mori et al. (2010) concluded that vaterite might be suitable as a coating to ink jet paper if formulated in a basic aqueous media where dissolution and re-precipitation as calcite is inhibited. It was explained by Meldrum and Colfen (2008) that vaterite forms polycrystalline spheres through the aggregation of nanoparticles, while Hu et al. (2012) showed how these spheres can develop into six-fold flower-like crystals after 16 hours.

5) Aragonite is the meta-stable and needle-shaped polymorph of CaCO₃. It is used commercially for specialized applications that require very high surface area, however the production of this polymorph requires relatively high temperatures (~70ºC).

6) Other commercial PCC crystal shapes are also produced, such as the rice-shaped synthetic calcium carbonate (CalciTech, 2015) and prismatic calcite (Eloneva 2010).
2.6.5 Particle Size Control

Gao et al. (2007) studied the influence of surfactants, mixing, reaction time and temperature on the particle size of calcium carbonate produced from distiller waste (15.28% CaCl$_2$, 10.11% NaCl) and mother liquor (7.31% NaCl, 6.43% (NH$_4$)$_2$CO$_3$, 16.58% NH$_4$Cl) from the Solvay process, i.e. the production of Na$_2$CO$_3$. Based on the spherical shape of the particles, it appears as though the authors produced polycrystalline vaterite spheres.

Their results show that the addition of surfactants had a significant influence on the average particle size; three surfactants were tested: cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl benzene sulfonate (SDBS), and Brij 35. CTAB and SDBS were more effective than Brij 35. Without the use of surfactant the mean particle size was $\sim$5.5 $\mu$m in diameter, and as low as $\sim$1.5 $\mu$m with surfactant.

Two different methods of combing the solutions were also tested. The first was “dropping” where the calcium chloride and ammonium carbonate solutions were quickly combined together in less than 30 seconds, and the second was “titrating” where the solutions were slowly combined over 100 seconds. In both cases, a reaction time of 30 minutes was used after the solutions were combined; the temperature was 20°C and 0.85 g/L of SDBS was used. The titration method was found to decrease the average particle size from 3.22 $\mu$m to 1.43$\mu$m.

Longer reaction times were found to increase the average particle size, from $\sim$2.75 $\mu$m after 30 minutes to $\sim$4.0 $\mu$m after 90 minutes (note: surfactants were also used in these experiments). Gao et al. (2007) explained this as the dissolution of fine particles and the growth of large particles, also referred to as Ostwald ripening.

Higher reaction temperatures (30 and 40°C) were found to significantly increase particle size, the authors explained this to be due to a high rate of particle growth and the integration of multiple particles. Reaction temperatures as low as 5°C did not produce notably smaller particles than those produced at 20°C.
Other authors (Meldrum and Colfen, 2008) stated that the concentration of CaCl$_2$ has a significant influence on the crystal morphology when CaCO$_3$ is precipitated via CO$_2$ bubbling. Vaterite particles of 1-2 µm were precipitated at low CaCl$_2$ concentrations (0.001 M), and the proportion of calcite and the size of the particles was found to increase with increasing CaCl$_2$ concentration (up to 0.5 M was tested). Higher [Ca$^{2+}$]/[CO$_3^{2-}$] ratios were said to favour calcite formation.

Rhombohedral calcite particles with a mean particle size of 0.6 µm were produced by Eloneva et al. (2008) by adding sodium hydroxide to a calcium acetate solution (producing calcium hydroxide), and then carbonating the calcium hydroxide by bubbling CO$_2$ through the solution.

### 2.7 Trace Element Leaching from Residual Products

A common concern regarding the production of PCC from industrial waste materials is that trace elements will be more soluble from the residual products than the original material. This was found to be the case with PCC production from steelmaking slag (Eloneva et al., 2010-b). Specifically, the authors found that up to 190 mg/kg of vanadium was water soluble from the residual products under shaking test (SPS-EN 12457-3),$^{22}$ compared to 0.06-0.2 mg/kg from the original material. Such issues with vanadium leaching are not expected to apply to waste concrete residues, because the vanadium content of steel converter slag was found to be ~1.35 wt.% (Eloneva et al., 2010-b). The authors also found that the solubility of chromium increased from 0.06-0.1 mg/kg in the original material to up to 1.1 mg/kg in the residual product. For reference, ALS Environmental (2016) stated that for granular waste acceptance at landfills, the total chromium ($\text{Cr}^{3+} + \text{Cr}^{6+}$) leaching limit is 0.5 mg/kg for inert waste, 10 mg/kg for stable

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$^{22}$ A liquid to solid ratio of 10 L per kg of material is used for the leaching test (ALS Environmental, 2016), and mg/kg is in reference to the amount of solute per kg of solvent (concentration).
non-reactive/non-hazardous waste, and 70 mg/kg for hazardous waste. Therefore the production of PCC from steelmaking slag may convert inert waste into a non-hazardous waste.

Some authors have noted that waste concrete contains hexavalent chromium (the more toxic oxidation state), and raised potential concerns regarding soil contamination (reviewed in CSI, 2009). On average, chromium levels in Portland cement are 76 mg/kg (Lea, 1970). For comparison, chromium levels in limestone are ~10 mg/kg, ~50 mg/kg in quartzite, ~200 mg/kg in basalt, and ~2,000 mg/kg in ultramafic rocks (Taylor, 1965). The CSI also reviewed that research in the UK by the Waste and Resources Action Programme found no difference, on average, between the trace element leaching behaviour of waste concrete and virgin materials. However, Swiss regulations were reviewed to prohibit the use of demolition materials for filtration and drainage bed applications due to potential contamination with chromium and pH-impact. Since it is a substituting trace element in iron and magnesium rich minerals, chromium levels in concrete might be mitigated if the use of mafic rocks as aggregates is avoided.

The leaching of chlorides from waste concrete (possibly sourced from road salt) and from residual materials of PCC production (especially were HCl is used as a solvent) is also relevant to the waste acceptance criteria at landfill. The limit for chloride leaching from inert waste is 800 mg/kg, 15,000 mg/kg for non-hazardous waste, and 25,000 for hazardous waste (ALS Environmental, 2016).
Chapter 3

Experimental Methods

The objectives of the experimental components of this work were to investigate the recovery of cement from waste concrete, the leaching of calcium by HCl, the purification of solutions before CaCO$_3$ precipitation, and the size and morphology of the CaCO$_3$. The methods used in these steps are described in this section. The CO$_2$ capture and chemical regeneration operations were not included.

3.1 Characterization of Waste Concrete Fines

It is important to analyze the fines that are recovered as a byproduct of crushing waste concrete in order to estimate the materials cement content (i.e. its uncarbonated calcium content), as this determines the carbon sequestration capacity. This step is necessary because under certain conditions waste cement has been shown to accumulate in the finest fractions (<500 µm). Additionally, some types of aggregates, such as limestone (CaCO$_3$), could have a significant impact on the carbon sequestration efficiency if they are crushed and are incorporated into the fines. This is because the calcium in limestone is already carbonated, and is readily dissolved in acidic solutions. Although the limestone could be upgraded to PCC, this does not result in carbon sequestration and inefficiencies inevitably produce fugitive CO$_2$ emissions.

The phrase “cement content” is used here to refer to the amount of uncarbonated calcium that is likely sourced from the main components of cement (hydrated calcium silicates, calcium hydroxide, calcium aluminate, and gypsum). In order to estimate the cement content of the waste concrete fines, several analytical methods were used: ICP-OES for chemical analysis, XRD to identify what crystalline phases were present, and TGA to quantify the carbonate content (wt% CO$_2$) and the Ca(OH)$_2$ content (wt% H$_2$O). Due to their amorphous nature, the calcium silicate components of cement usually cannot be identified by XRD (Lea, 1998, p. 250), however their
presence is inferred when there is an excess of calcium relative to the carbonate content (wt% CO₂), and no other calcium phases are prevalent enough to account for the excess calcium.

Dolomite (CaMg(CO₃)₂) is a type of altered limestone, and was identified in every sample, and was the only magnesium mineral that showed strong peaks in the XRD pattern. Calcite (CaCO₃), portlandite Ca(OH)₂, and quartz (SiO₂) were also identified in each sample; no other crystalline calcium minerals were identified in any of the fines. Therefore, the fraction of uncarbonated calcium (i.e. cement-calcium) was estimated as follows:

First, the moles of Ca and Mg (per gram of fines) were quantified by ICP-OES, and were assumed to be the only carbonated metals. Then the moles of CO₂ per gram of fines were quantified by TGA. The moles of CO₂ associated with dolomite (CaMg(CO₃)₂) was estimated as two times the moles of magnesium, since dolomite appeared to be the only significant source of magnesium, and for every mole of magnesium there is one mole of calcium in dolomite. The CO₂ remaining after dolomite accounting was assumed to be associated with calcite (CaCO₃).

The moles of calcium remaining after dolomite and calcite accounting was said to be uncarbonated calcium sourced from cement. While the calcium hydroxide content was quantified by TGA, the hydrated calcium silicate and gypsum (CaSO₄·2H₂O) content could not be quantified separately. The sulfur content was quantified through ICP-OES, but as other likely sources of sulphur exist, such as iron sulphide in the limestone aggregates (Gillott, 1963), therefore the sulphur content could not be taken as an indication of gypsum content.

After crushing and sieving the waste concrete, the fraction of cement recovered in the fines (Dp<425 μm) from the original mass of waste concrete was estimated as:

\[
\text{\% cement recovered} = \left( \frac{\text{(mass of fines (wt\%) × (wt\% uncarbonated Ca)}}{\text{(mass of original concrete (100\%) × (5\% uncarbonated Ca)}} \right) \times (100\%) \tag{3.1}
\]

Waste concrete was estimated to contain 5.0% uncarbonated calcium from the cement component alone because Tam et al. (2007) reviewed that cement contains ~46% calcium by mass, and concrete contains ~11% cement by mass (Portland Cement Association, 2015).
3.1.1 Materials, Crushing and Sieving

Two distinct types of waste concrete were used in this study. The first type was named “high carbonate concrete” (HCC) and was obtained by retrieving boulders (Dp≈25cm) of waste concrete that were to be utilized as earth fill on the grounds of the Royal Military College of Canada (RMC) in Kingston, Ontario. The second type of waste concrete was named “low carbonate concrete” (LCC) and boulders were retrieved from the waste pile from the concrete strength testing facility of the Civil Engineering Department at RMC. The aggregate composition was significantly different between the two concrete types. This was believed to have a significant influence on the CO₂ sequestration potential of the fines. The HCC contained mostly carbonate aggregates, and the LCC contained mostly igneous and metamorphic aggregates. The boulders of waste concrete were reduced to smaller particles (Dp≈10cm) via sledge hammer so that the particles could be fed into a jaw crusher. A mass of approximately 5-8 kg of each concrete type was processed by the jaw crusher, and the fines were sieved. Eight different sieve sizes (<105, 105-425, 425-1000, 1000-1400, 1400-2360, 2360-3327, 3327-5000, and 5000-10000 µm) were stacked and a mechanical shaker that was used to shake the stack for 5 minutes. The particle size distribution of the waste concrete fines was determined by measuring the mass contained in each sieve.

3.1.2 Quantitative Elemental Analysis of Solids: ICP-OES

Quantitative elemental analyses on the waste concrete fine fractions (Dp<105 µm and 105 µm<Dp<425 µm) were done by inductively coupled plasma optical emission spectrometry (ICP-OES). A mass of 0.5g of the solid was dissolved in aqua regia (a mixture of HNO₃ and HCl) at 90°C overnight before the solutions were filtered and analyzed. The term “elemental analysis” can be better described as an analysis of the extractable metals. This is because silicon is a significant component of concrete as it present in quartz sand and in cement, but the nitric and hydrochloric acids in aqua regia do not sufficiently dissolve silicon for it to be quantified.
The silicon content could have been quantified if hydrofluoric acid was also added, and the mixture was later cooked with boric acid in an inert Teflon container and the ICP was switched out with an inert sample introduction system. This was not believed to be necessary because metal leaching with HCl was the main focus of the experimental program.

3.1.3 Phase Identification: XRD

Crystalline minerals in the waste concrete fines were also identified using X-Ray Diffraction (XRD). Reitveld Analysis was considered for quantifying the amount of each phase but was ruled out because of amorphous content in the solids (which interferes with the quantitative analysis). The XRD results are presented in Appendix D.

3.1.4 Quantifying Hydroxide and Carbonate Phases

The carbonate and hydroxide content of the solids were quantified by thermogravimetric analysis (TGA) using TA Instruments model Q-50. The solids were finely ground by mortar and pestle until they appeared to be homogeneous and free of grit before analysis. The flow rate of nitrogen for the balance was 40ml/min, and the flow rate of nitrogen going into the furnace was 60ml/min. A heating rate of 10ºC/min was used for every sample. A titanium pan was used, and 15-20mg of sample was loaded onto the pan for analysis. XRD was used to assist in phase identification due to overlapping thermal decomposition curves between possible phases (e.g. the partial overlap of dolomite and calcite thermal decomposition).

The first step in quantifying the carbonate and hydroxide mineral content was to analyze pure phases and plot the rate of mass loss vs. temperature (Figure 3.1). From Figure 3.1 it can be seen that the thermal decomposition curves of pure calcium carbonate and pure dolomite have some overlap; both of these minerals were found to be present in the waste concrete fines by XRD; therefore they cannot be individually quantified by TGA alone (Bigham et al., 2005). The combined carbonate content of calcium carbonate and dolomite can still be quantified by
measuring the wt.% loss over the calcination curve (~550-800°C); the mass loss is due to CO₂ being released from the solids.

Figure 3.1: Thermal analysis curves of pure phases.

The precise temperature range of calcination varied slightly between samples, particularly between the reagent grade CaCO₃ (Figure 3.1) and the waste concrete fines (Figure 3.2). Variations in the calcination temperature range can be explained by different particle size distributions, different crystal structures of CaCO₃ (amorphous, aragonite, calcite and vaterite), and different amounts of CaCO₃ vs. CaMg(CO₃)₂; Ramachandran et al. (2002, p.76) also stated that impurities lower the activation energy.

Some Mg(OH)₂ and MgCO₃ may be present in the concrete from the hydration and subsequent carbonation of magnesium-based cement, however this should not be a significant source because most cement producers favor an upper limit of 3% MgO in the clinker (reviewed in Oates, 1998, p.82). Another possible source of Mg(OH)₂ and MgCO₃ could be from dolomite aggregate via the alkali-carbonate reaction in concrete (a known degradational process) which was described in Kingston, Ontario (Gillott, 1964) as:
CaMg(CO$_3$)$_2$ + 2NaOH → Na$_2$CO$_3$ + Mg(OH)$_2$ + CaCO$_3$  \hfill (3.2)

An overlap in the TGA curves of MgCO$_3$ and Ca(OH)$_2$ at ~400°C is also shown in Figure 3.1, the TGA peak at this temperature in the waste concrete fines is assumed to be only from Ca(OH)$_2$ because it was identified by XRD while MgCO$_3$ was not, and Ca(OH)$_2$ is produced by the hydration of cement:

\[
2[3\text{CaO} \cdot \text{SiO}_2] + 6\text{H}_2\text{O} \rightarrow [3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}] + 3\text{Ca(OH)}_2 \tag{3.3}
\]

The mass loss over the Ca(OH)$_2$ curve is from the release of H$_2$O, therefore the Ca(OH)$_2$ content can be calculated as:

\[
\text{wt}\% \text{Ca(OH)}_2 = (\text{wt}\% \text{H}_2\text{O loss}) \times (74.09 \text{g/mol Ca(OH)}_2 / 18.02 \text{g/mol H}_2\text{O}) \tag{3.4}
\]

The mass loss below 300ºC in the waste concrete fines can be explained by the removal of water from hydrated minerals such as gypsum (CaSO$_4$·2H$_2$O), ettringite (Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{12}$·26H$_2$O), or C-S-H (3CaO·2SiO$_2$·3H$_2$O) (Dilnesa, 2015). A summary of the TGA peak identities in the waste concrete fines is shown in Figure 3.2.

Figure 3.2: Differential Thermal analysis curves of low and high carbonate concrete fines (Dp<105 µm) with peak identifications.

The mass loss between ~450-600ºC, i.e. between the Ca(OH)$_2$ peak and the well-defined calcination peak was initially considered to be CO$_2$ being released from amorphous carbonates or
carbonates with finer crystalline structure based on analysis of cement kiln dust (Huntzinger 2006). However, after comparing the TGA results with the elemental analysis (ICP-OES) of the high carbonate concrete fines, it is unlikely that in this case the mass loss between ~450-600°C is due to CO\textsubscript{2} sublimation. This is because the ICP-OES results suggest a ~20% excess of CO\textsubscript{2} relative the calcium and magnesium in the high carbonate concrete if the mass loss between 450-600°C is interpreted as CO\textsubscript{2} loss (Appendix I). Another explanation is the loss of SO\textsubscript{2} due to the oxidation and decomposition of trace amounts of pyrite (iron sulphide). Hansen et al. (2003) stated that the oxidation of pyrite by heating is the main source of SO\textsubscript{2} emission from cement manufacturing, and that it occurs at around 400-600°C. Pyrite is a common trace element in many rock types, including limestone (Oates, 1998). If 1.6% of the mass was lost as SO\textsubscript{2} from (Table 3.1), this can be converted to 0.78% wt. S, which is slightly greater than 0.63% S measured by ICP-OES (which might have underestimated S content due to H\textsubscript{2}S loss). If 0.78% wt. S was associated with pyrite (FeS\textsubscript{2}) in the LCC fines, it would account for ~60% of the iron in the material,\textsuperscript{23} which seems reasonable. However, it is difficult to accept that pyrite is being oxidized because the chamber was continuously purged with nitrogen. Therefore the mass between ~450-600°C remains unidentified, but is unlikely to be CO\textsubscript{2} loss.

To quantify the CO\textsubscript{2} and calcium hydroxide content of the waste concrete fines, the samples were analyzed by TGA in triplicates. As an example, the analyses for the Dp<105 μm fraction from the low carbonate concrete are shown below:

\textsuperscript{23} 1.1% wt total Fe measured by ICP-OES (Appendix C)
3.2 Leaching Experiments with HCl and waste concrete

The objective was to leach 100% of the non-carbonated calcium from the waste concrete. In the leaching experiments, the two finest size fractions of the crushed waste concrete (105µm<Dp<425µm and Dp<105µm) were tested separately for both the high and low carbonate concrete fines. For all experiments a 0.54M ± 0.006M hydrochloric acid solution was used; the solution was diluted from 12.1M HCl (Fisher Scientific) and was standardized first by standardizing a NaOH solution with oven-dried potassium hydrogen phthalate in triplicate, and then using the NaOH to determine the HCl concentration by titration in triplicate.

The waste concrete fines were added to the hydrochloric acid solutions in a 500ml Erlenmeyer flask, and mixed for 2 hours at ambient conditions with a magnetic stir bar at 400 rpm. The pH of the solution was monitored with a pH meter (Accument Basic, AB15) and pH probe (Accument, 13-620-530A). After 2 hours of mixing, 25ml of solution was taken and filtered through a syringe with a 0.45µm filter; these solutions were later analyzed by ICP-OES. The 25ml samples were digested with nitric acid/HCl/water at 90°C just before ICP-OES in order to detect cations that had precipitated while the solutions were stored in glass vials. Silicon was not analyzed for reasons similar to those described in the previous section. The ICP-OES results
were obtained in terms of molality (µg/g of solution) and a solution density of 1.0 g/mL was estimated to convert to molarity (µg/mL of solution).

3.3 Purification of CaCl₂ Solutions

After the aliquot was taken for ICP-OES, the remaining solution was filtered with a Buchner funnel under vacuum with Fisher brand P2 filter paper. Once filtered, a 100 ± 0.08 mL aliquot was taken by pipette. The threshold for purification was pH 9.0 after 2 hours of mixing; solutions with a pH greater than 9.0 did not require a separate purification step. The 100 mL of solution was placed in a 150mL beaker, mixed at 600 rpm with a magnetic stir bar, and a drop of phenolphthalein indicator was added as a visual aid. A mass of Ca(OH)₂(s) in a weighing tin was measured and was slowly added to the solution, until a pH of 9.0±0.1 was reached as determined by pH probe. The mass of Ca(OH)₂(s) added to the 100mL of solution was determined by measuring the mass difference using a Mettler Toledo XS205 balance (± 0.01 mg). Once the pH of the solution was observed to remain stable at pH 9 for 10 minutes, the solution was filtered again with a cone filter under vacuum with Fisherbrand P2 filter paper. After the purified solution was filtered another 25 mL aliquot was taken and filtered with a 0.45µm syringe filter for ICP-OES.

The solid concrete residue in the Buchner funnel was washed with 100 mL of deionized water. The washed residue was then filtered and the mass of the solids was recorded. This concrete residue was then dried for 2-3 days at 110ºC, and the dried mass was then weighed. Finally, the dried concrete residue was analyzed by TGA, and the carbonate content was determined as described in section 3.2.1. The mass of CO₂ in the concrete residue could then be determined by the (m_{residue}) x (wt% CO₂). The purification waste solids in the cone filter were rinsed with deionized water to remove chlorides, then dried for 2-3 days at 110ºC, weighed, and analyzed by TGA and EDAX.
3.4 Precipitation of Calcium Carbonate

After the pH ≥ 9 solutions were filtered with Fisherbrand P2 filter paper, aliquots of 25 ± 0.03 mL were taken by pipette and placed in a 150 mL Erlenmeyer flask with a magnetic stir bar set to 400 rpm. While the solution was being stirred, 25 ± 0.03 mL of 0.26 M ± 0.008 M Na₂CO₃ was added by pipette. The Na₂CO₃ concentration was determined by titrating 25 ± 0.03 mL of Na₂CO₃ solution with 0.54 M ± 0.006 M HCl as ½ the moles of HCl required to titrate between two inflection points (pH 8.3 and 3.45). Adding the Na₂CO₃ in this manner was chosen because it has been shown that smaller particles of calcium carbonate precipitated when CaCl₂ and (NH₄)₂CO₃ solutions were slowly mixed vs. dumping (Gao et al., 2007). The solutions were mixed for 30 minutes before being filtered with Fisherbrand P2 filter paper in a cone filter under vacuum to recover the precipitated calcium carbonate; 25 mL of solution was then taken for ICP-OES after being filtered with 0.45µm syringe filter. The precipitated calcium carbonate was rinsed and then dried for 2-3 days at 110ºC before measuring the dry mass and analyzing it by TGA. DTA peaks at approximately 400ºC for the PCC samples were interpreted to be MgCO₃; other peaks were identified as described in section 3.2.1. A mixing time of 30 minutes was used because Gao et al. (2007) also showed that longer times at 20ºC increased the average particle size from ~2.75 µm to ~4.0 µm.
Chapter 4

Results and Discussion

4.1 Material Characterization

4.1.1 Mass Recovered as Fines (Dp<425 µm)

The particle size distribution of the crushed waste concrete is presented in Table 4.1, it can be seen that 8.3% of the low carbonate concrete (LCC) was recovered in the Dp<425 µm fraction, and 9.0% from the high carbonate concrete (HCC). These fine fractions (Dp<425 µm) are studied in the leaching experiments in this thesis, while the coarser fractions of the crushed waste concrete might be suitable for road (sub)base, or ground to the same size for leaching. It is likely that some of these larger fractions contain waste cement bound to the particle surfaces and an additional exfoliation or leaching step may recover additional calcium for CO₂ sequestration and improve the quality of the aggregate produced in this manner.

Table 4.1: Particle size distribution of crushed waste concrete.

<table>
<thead>
<tr>
<th>particle size (µm)</th>
<th>LCC mass (%)</th>
<th>HCC mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000-5,000</td>
<td>37.59</td>
<td>38.57</td>
</tr>
<tr>
<td>5,000-3,327</td>
<td>22.21</td>
<td>22.47</td>
</tr>
<tr>
<td>3,327-2,360</td>
<td>9.65</td>
<td>8.49</td>
</tr>
<tr>
<td>2,360-1,400</td>
<td>9.38</td>
<td>8.88</td>
</tr>
<tr>
<td>1,400-1,000</td>
<td>4.31</td>
<td>4.64</td>
</tr>
<tr>
<td>1,000-425</td>
<td>8.56</td>
<td>7.94</td>
</tr>
<tr>
<td>425-105</td>
<td>6.48</td>
<td>6.60</td>
</tr>
<tr>
<td>&lt;105</td>
<td>1.82</td>
<td>2.42</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

4.1.2 CO₂ Sequestration Capacity of Waste Concrete Fines

In addition to recycling waste, one of the objectives of this process is to sequester CO₂. In order to estimate the CO₂ sequestration capacity, the amount of uncarbonated calcium and magnesium is calculated by first measuring the total amount of calcium and magnesium, and then subtracting amount
associated with CO\(_2\) (i.e. the amount that is already carbonated). All of the magnesium was assumed to already be carbonated because dolomite (CaMg(CO\(_3\))\(_2\)) was the only magnesium mineral that showed well defined peaks in the XRD pattern (Appendix D). Additionally, the magnesium content of Portland cement is constrained to approximately 0.7% wt. Mg (Iizuka, 2006), thus limiting the amount of amorphous magnesium silicate cement phases that would not be detectable by XRD. Therefore in this case, the amount of uncarbonated calcium per mass of material can be estimated with Equation 4.1. This equation estimates the uncarbonated calcium content as the molar sum of calcium and magnesium, minus the moles of CO\(_2\) (i.e. the moles of carbonate), and assumes all the magnesium is carbonated. The results and analysis of the CO\(_2\) sequestration capacity of the waste concrete fines (Dp<425 µm) are presented in Table 4.2.

\[
\text{mmols Ca uncarbonated} = \left( \frac{\text{mmols Ca}}{100 \text{ g}} + \frac{\text{mmols Mg}}{100 \text{ g}} \right) - \left( \frac{\text{mmols CO}_2}{100 \text{ g}} \right) \quad (4.1)
\]

From Table 4.2 it can be seen that while the content of Ca and Mg in the LCC and HCC materials were relatively similar, the carbon sequestration capacity of the materials were dramatically different. Approximately 70-74% of the calcium was uncarbonated in the LCC fines, while only 13-19% of the calcium was uncarbonated in the HCC fines. The accumulation of cement particles within the LCC fines can be explained by the exfoliation of cement from strong igneous and metamorphic aggregates during the crushing process, while the aggregates themselves were not sufficiently pulverized to be incorporated into the fines as significantly. If crushed dolomite aggregate is the only significant source of magnesium, then a higher Ca:Mg molar ratio logically indicates a higher cement:crushed aggregate ratio.

The LCC aggregates were visually inspected and consisted of gravel that was a mixture of gneiss (W\(_i\) = 22.19), syenite (W\(_i\) = 14.47), quartzite (W\(_i\) = 17.4), with a relatively small amount of limestone/dolomite (W\(_i\) ≈ 12); for review the W\(_i\) values represent the work required to crush the materials (kWh/tonne) and were retrieved from Table 2.1. The W\(_i\) value for raw cement was listed as 11.59, which is similar to that of limestone/dolomite, however additives such as fly ash are sometimes used to make high-strength cement. The relatively small amount of carbonate aggregates in the LCC helps to explain...
why ~30% of the calcium was carbonated, some CaCO$_3$ was likely produced via passive carbonation as well.

The HCC fines appear to contain mostly pulverized limestone and dolomite aggregate, where most of the uncarbonated calcium is accounted for calcium hydroxide. The predominance of pulverized carbonate aggregates in the fines is explained by their lower physical strength ($W_i$), and being of sedimentary origin they were likely broken into a powder rather than breaking into larger fragments as with stronger igneous and metamorphic aggregates in the LCC (quartzite, syenite and gneiss). Some of the aggregates in the HCC (before crushing) were also observed to be significantly larger than those in the LCC, this likely contributed to the results. Passive carbonation may also help explain the results, particularly if the concrete was of low compressive strength (Lagerbald, 2005) and thickness (i.e. if it was sourced from a demolished sidewalk, for example). The relatively high calcium hydroxide content of the HCC fines (12-16% of the calcium) is counter-intuitive at first, however previous authors have noted that calcium hydroxide is concentrated at the cement-aggregate interface (Zimbelmann, 1985), this could explain how it was incorporated into the fines with the crushed aggregate.

The end result is that the high carbonate concrete, as crushed and analyzed in this work, is less suitable for CO$_2$ sequestration due to low cement recovery. There is potential that cement recovery in the HCC fines could have been improved by reducing the extent of crushing to help preserve the carbonate aggregates as large particles. The fine fraction of the LCC material shows promise, as it is able to sequester ~13% of its own weight as CO$_2$ (Table 4.2). This can be converted to 1.1% of the mass of the original waste concrete, since the LCC fines (Dp<425 µm) consisted of 8.3% of the original mass (Table 4.1).
Table 4.2: Analysis of the CO$_2$ sequestration capacity of waste concrete fines.

<table>
<thead>
<tr>
<th></th>
<th>Low Carbonate Concrete (LCC)</th>
<th>High Carbonate Concrete (HCC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Dp&lt;105\mu m$</td>
<td>$105\mu m&lt;Dp&lt;425\mu m$</td>
</tr>
<tr>
<td><strong>Wt% from ICP-OES analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>Mg</td>
<td>2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Ca:Mg molar ratio</td>
<td>3.7:1</td>
<td>4.6:1</td>
</tr>
<tr>
<td><strong>Wt% from TGA Analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>10.75 ± 0.21</td>
<td>7.84 ± 0.26</td>
</tr>
<tr>
<td>Ca(OH)$_2$</td>
<td>4.20 ± 0.13</td>
<td>2.60 ± 0.10</td>
</tr>
<tr>
<td><strong>CO$_2$ Sequestration Capacity per 100 g</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mmoles Ca</td>
<td>424.17</td>
<td>374.27</td>
</tr>
<tr>
<td>mmoles Mg</td>
<td>115.20</td>
<td>82.29</td>
</tr>
<tr>
<td>mmoles CO$_2$</td>
<td>244.26</td>
<td>178.14</td>
</tr>
<tr>
<td>mmol Ca uncarbonated</td>
<td>295.11</td>
<td>278.42</td>
</tr>
<tr>
<td>%Ca uncarbonated</td>
<td>69.57</td>
<td>74.39</td>
</tr>
<tr>
<td>wt% uncarbonated Ca</td>
<td>11.8</td>
<td>11.2</td>
</tr>
<tr>
<td>%Ca as Ca(OH)$_2$</td>
<td>13.35</td>
<td>9.34</td>
</tr>
<tr>
<td>kg CO$_2$/tonne fines</td>
<td>130</td>
<td>122</td>
</tr>
</tbody>
</table>

Elemental analysis was done by ICP-OES; wt% CO$_2$ and wt% Ca(OH)$_2$ were quantified by TGA ± values represent the standard deviation of triplicates and are expressed as wt%

4.1.3 Cement Recovery Efficiency

With Equation 3.1 the amount of cement recovered from the original waste concrete as fines ($Dp<425\mu m$) was estimated from the uncarbonated calcium content of the fines. From Table 4.3 it can be seen that 18.8% of the cement is estimated to have been recovered in only 8.3% of the mass of the crushed low carbonate concrete. This means that through the recovery process the cement content of the fines was enriched by ~225% relative to the composition of unprocessed concrete (Figure 1.1). However, with the HCC, only 5.2% of the cement was recovered in 9.0% of the mass, meaning that the cement content was either diluted with crushed
aggregates through the recovery process, or that passive carbonation was extensive, or a combination of the two.

Table 4.3: Cement recovery in the fines (Dp<425 µm) of crushed waste concrete.

<table>
<thead>
<tr>
<th>Size Fraction</th>
<th>Low Carbonate Concrete (LCC)</th>
<th>High Carbonate Concrete (HCC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dp&lt;105µm</td>
<td>1.82 %</td>
<td>2.42 %</td>
</tr>
<tr>
<td>105µm&lt;Dp&lt;425µm</td>
<td>6.48 %</td>
<td>6.60 %</td>
</tr>
<tr>
<td>Mass of Fines</td>
<td>11.8 %</td>
<td>2.5 %</td>
</tr>
<tr>
<td>Uncarbonated Calcium</td>
<td>11.2 %</td>
<td>2.5 %</td>
</tr>
<tr>
<td>Cement Recovered</td>
<td>4.30 %</td>
<td>14.52 %</td>
</tr>
</tbody>
</table>

4.2 Leaching Calcium from Waste Concrete Fines

4.2.1 pH and Dissolved Elements

Batches of waste concrete fines were dissolved in various volumes of 0.5 M HCl for 120 minutes while the solution pH was periodically monitored. Two particle size fractions were tested from each concrete type. The HCl:(Ca+Mg) ratio (i.e. the ratio between the moles of acid added to the moles of the main acid-neutralizing elements in the solids) varied between 0.4 and 2.4, where 2.0 is the stoichiometric amount to dissolve all the calcium and magnesium (Ca+Mg) by HCl.

The HCl:(Ca+Mg) ratio had the strongest influence on pH, while particle size appeared to have a minor influence pH (Figure 4.1). With the finest particles the solution pH almost immediately increased to ≥ 10.0 when the HCl:(Ca+Mg) ratio was ≤ 0.5; however with the coarse particles the pH slowly increased from ~7.0 to 10.0 under similar conditions. With these low HCl:(Ca+Mg) ratios, the solution pH appears to be controlled by the dissolution of residual alkaline minerals after the HCl has been neutralized. Figure 4.2 shows that alkaline, neutral and

---

24 Wt% of original concrete recovered in a given size fraction
25 Calculated as the %wt Ca multiplied by the %Ca uncarbonated (Table 4.2)
26 % cement recovered from original concrete (Equation 3.1)
acidic solutions are likely to be produced when the HCl:(Ca+Mg) ratio is approximately 0.5, 1.0, and 2.0 respectively.

![Figure 4.1: Solution pH over time during the leaching experiments with HCC and LCC fine (a) and coarse (b) particles. The numerical values represent the HCl:(Ca+Mg) ratio.](image)

From Figure 4.1 (a) and Figure 4.2 it can be seen that the fine (Dp<105 µm) LCC materials produced more alkaline solutions than the fine HCC materials. Bulk pulverized (BP) HCC materials (Dp<105 µm) are also included in the Figure 4.2. Since the low carbonate concrete (LCC) contains more cement, it might be possible for any residual unhydrated cement to
hydrate and produce Ca(OH)₂ after HCl neutralization. However the XRD results do not support this since significant levels of unreacted cement (alite, belite, and etc.) were not identified (Appendix D). If present in significant amounts, these unreacted cement phases should be detectable by XRD (Lea, 1970). Another suspected cause was the lower reactivity of dolomite in the HCC with HCl compared to the cement in the LCC, however, this also does not appear to be a likely explanation because Figure 4.4 suggests that Ca+Mg leaches from HCC and LCC with equal efficiency.

The (aqueous) oxidation of pyrite (FeS₂) in the HCC materials might be a more likely explanation for the more acidic solutions produced with HCC fines. The HCC materials could contain more pyrite because they contain more natural limestone/dolomite; the dark colour of limestone/dolomite can often be attributed to traces of pyrite (Oates, 1998; Gillott, 1963). Furthermore, the LCC likely has less pyrite because it is mostly cement, and pyrite oxidizes to SO₂ and Fe₂O₃ when cement-kiln feed is heated. This is the primary source of SO₂ emissions during cement manufacturing (Hansen et al., 2003). The (aqueous) oxidation of pyrite occurs in several main steps (Equation 4.2-4.4), and is summarized by Equation 4.5. Of note is that the main acid generating step is the hydrolysis of Fe³⁺ and precipitation of Fe(OH)₃, shown in Equation 4.5 (Dold, 2014). The solubility of Fe³⁺ is significantly less than that of Fe²⁺, as was described in Figure 2.6.

\[
\begin{align*}
\text{FeS}_2 + 7/2\text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad (4.2) \\
\text{Fe}^{2+} + 1/4\text{O}_2 + \text{H}^+ & \leftrightarrow \text{Fe}^{3+} + 1/2\text{H}_2\text{O} \quad (4.3) \\
\text{Fe}^{3+} + 3\text{H}_2\text{O} & \leftrightarrow \text{Fe(OH)}_3(\text{s}) + 3\text{H}^+ \quad (4.4) \\
\text{FeS}_2 + 15/4\text{O}_2 + 7/2\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad (4.5)
\end{align*}
\]
Figure 4.2: The solution pH after 120 minutes of leaching v.s. acid neutralizing potential with various concrete types and size fractions.

Aliquots of solution were taken at the 120 minute mark, and the concentration of dissolved elements (ICP-OES results) vs. pH is shown in Figure 4.3. Here it can be seen that the solution pH can reflect the concentration of impurities in solution, therefore metals such as iron are likely removed from solution as the solution pH increases over time. Although some residual HCl may be present in the acidic solutions, Fe, Al, Mn and Zn ions can also influence pH by forming aquo-complexes and acting as weak acids through the repulsion of protons in the water molecules of their solvation shells (White, 2013). These metals also contribute to acidity by acting as a pH buffer when alkalinity is added (Hughes and Grey, 2013). The dissolved sulphur might also influence pH through the conversion of sulphate into H₂S (a slightly soluble gas) in acidic and reducing environments through its dissociation to HS⁻ and H⁺ (pKa = 7.0). This speculation is based on the observation of H₂S odour during experiments, which could be an indication of reducing conditions.
From Figure 4.3 it can be seen that the solubility of magnesium appears to be controlled by the solubility of Mg(OH)$_2$. It should be noted that the results in Figure 4.3 represent individual leaching experiments that were conducted by adjusting the HCl:(Ca+Mg) ratio, and do not represent the progressive removal of impurities from an acidic solution by adding alkalinity. In such a case, the removal of impurities is not expected to follow the same trend because of silica leaching at higher HCl:(Ca+Mg) ratios (Shuto et al., 2014), and the subsequent precipitation of silicates instead of hydroxides as pH increases. The alkaline solutions in Figure 4.3 were produced by using HCl:(Ca+Mg) ratios below 0.5, where Ca(OH)$_2$ and CaCO$_3$ may have been preferentially leached without leaching significant amounts of silica.

The concentration of iron and manganese in solution are important because they readily discoulour PCC (Teir et al. 2005). Although ferrous iron is significantly more soluble than ferric iron (Figure 2.6), ferrous iron can become oxidized by oxygen and precipitate as ferric hydroxide (Equation 4.4). The solid purification residue produced by increasing the pH of the solutions...
from pH ~4.0 to ~9.0 had a noticeable green rust colour, which later turned to a red-rust colour after continued exposure to air; this suggests that ferrous iron was leached (likely from pyrite). Ferrous iron it is known to oxidize at high temperatures in the cement kiln (Hansen et al., 2003), therefore crushed limestone aggregates (containing small amounts of pyrite) may be a more likely source of ferrous iron than cement.

A longer leaching time of 24 hours was also investigated in preliminary experiments, and although a neutral pH was reached after 24 hours when the pH after 2 hours was 5.7, the filtration of the solution was noticeably inhibited. This was interpreted to be due to the formation of a silica gel from colloidal silica (Espíari et al., 2006). This phenomena was also observed by other authors (Eloneva, 2010).

The odour of H$_2$S was noticed to evolve from acidic solutions. The sulphur could have been dissolved from either pyrite or gypsum, and the formation of H$_2$S is known to be favoured in acidic and reducing environments. No odor was observed when the solution was not acidic, suggesting the sulphur was contained in solution as sulphate. The concentration of sulphate is likely controlled by the solubility of gypsum given the excess of calcium in solution. Furthermore the common ion effect from CaCl$_2$ diminishes the solubility gypsum (Li and Demopoulos, 2005). Li and Demopoulos calculated the solubility of gypsum to be ~0.008 mols/kg (log M = -2.1) in 0.25 M CaCl$_2$, this could explain the measured sulphur levels.

4.2.2 Extraction Yield

The extraction yield (or leaching efficiency) represents the amount of an element leached relative to the total amount in the feed material, a summary of the chemical analysis of the feed materials is shown in Table 4.4. Figure 4.4 shows how the HCl:(Ca+Mg) ratio influences the extraction yield of Ca, Mg, Fe, Mn, Al and S from waste concrete fines after 2 hours of leaching. Fe and Mn both discolor PCC, and although the Mn wt% content was ~10-20 times less than that of iron, its hydroxide is over 200 times more soluble than that of ferrous iron (Figure 2.6). A
The discussion of Ba leaching is included due to its toxicity and incorporation into the PCC.

Although not shown, mineralogy was an additional difference (the carbonate vs. silicate content).

The results suggest that the extraction of most elements (especially calcium and magnesium) follow the same general trend despite the differences in mineralogy.

Table 4.4: Summary of chemical analysis on waste concrete fines.

<table>
<thead>
<tr>
<th></th>
<th>Low Carbonate Concrete (LCC)</th>
<th>High Carbonate Concrete (HCC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Dp&lt;105\mu m$</td>
<td>$105\mu m&lt;Dp&lt;425\mu m$</td>
</tr>
<tr>
<td><strong>ICP-OES analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ca (wt%)</strong></td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td><strong>Mg (wt%)</strong></td>
<td>2.8</td>
<td>2</td>
</tr>
<tr>
<td><strong>Fe (wt%)</strong></td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Mn (wt%)</strong></td>
<td>0.12</td>
<td>0.084</td>
</tr>
<tr>
<td><strong>Al (wt%)</strong></td>
<td>1.9</td>
<td>1.4</td>
</tr>
<tr>
<td><strong>S (wt%)</strong></td>
<td>0.63</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The extraction of calcium followed a linear trend and reached ~100% when the HCl:(Ca+Mg) ratio reached ~2:1. Extraction yields of ~110% can be explained by sample variability. Calcium was selectively dissolved from magnesium when the HCl:(Ca+Mg) ratio was below ~0.6:1, this can be explained by the preferential dissolution of the more reactive minerals Ca(OH)$_2$ (portlandite) and CaCO$_3$ (calcite). The extraction yield of magnesium reached ~40% when all the calcium was dissolved. This suggests Mg will be preferentially left in the solid phase, aiding the production of high purity CaCO$_3$.

From Figures 4.4 (c) and (d) it can be seen that iron begins to dissolve when the HCl:Ca+Mg ratio exceeds ~1, and that manganese dissolves more readily. The leaching of these metals, even at low concentrations can be detrimental to the brightness of PCC. The outlier in the extraction yield of manganese in the LCC fines when the HCl:Ca+Mg ratio was ~1 is explained by the anomalously high pH of the solution (pH~9 v.s. pH~7), as shown in Figure 4.2. 
Figure 4.4: The extraction yield of various elements from different materials v.s. the HCl:(Ca+Mg) ratio. The legend in (a) applies to all graphs in the series, and the Ca:Mg ratio applies to the description of each material. 15.0g of waste concrete fines and various volumes of 0.5 M HCl were used, the solutions were stirred at 400rpm for 120 minutes before sampling.
A low (<3%) extraction yield of aluminum was maintained when the HCl:Ca+Mg ratio was below 2:1, however it then sharply increased when an excess of HCl was added and the solution pH decreased. The concentration of aluminum in solution is likely controlled by the solubility of Al(OH)$_3$ and kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), which are insoluble in near-neutral waters, i.e. pH=7 (White, 2013).

Approximately 25% and 50% of the sulphur was dissolved when the HCl:Ca+Mg ratio was ~0.5:1 and ~1:1 respectively. Beyond this it appears as though the linear trend starts to diverge. Based on the observation of H$_2$S odor at higher HCl:Ca+Mg ratios and lower pH values, it is believed that the linear trend is broken due to liberation of sulphur from solution through the formation of H$_2$S gas under more acidic and reducing conditions. If a high calcium extraction efficiency is desired then measures to manage the fumes should be implemented. The use of oxidizing agents (ideally oxygen) might be an option to help prevent H$_2$S fumes, provided than chloride is not also oxidized. In all cases sulphur accounted for a notable mass fraction of the dissolved elements, however its precipitation in the Na$_2$CO$_3$ addition step was not anticipated. This is because the solubility of gypsum should increase during CaCO$_3$ precipitation because the common ion effect is being removed, and also the sulphate is diluted by the addition of Na$_2$CO$_3$(aq).

The barium content of PCC is sometimes listed in the material analysis done by a distributor, and the limit for the barium content in pharmaceutical grade PCC was stated to be 20 ppm (Caltron-Clays, 2015). The content of this element in PCC is likely constrained because BaCO$_3$ is toxic and is often used as rotenticide (Ghose et al., 2009). The barium content in the waste concrete fines was found to be up to 320 ppm (µg/g) in the finest size fraction of the LCC samples (Appendix C). If all of this barium was leached as BaCl$_2$ when 25% of the calcium was leached (75 mL of 0.25M CaCl$_2$), then the maximum barium content of the CaCO$_3$ can be estimated to be 2,560 ppm (4.8 mg B/1,875 mg PCC).
Therefore if all the barium was leached and precipitated with CaCO$_3$, then the CaCO$_3$ might be considered hazardous. However, less than 4% of the barium was leached when 25% of the calcium was leached from the high-Ba materials (LCC). This still suggests a maximum barium concentration of 102 ppm in the CaCO$_3$. The barium leaching efficiency increased to ~20% when all the calcium was leached from the LCC fines (Appendix L), meaning the Ba:Ca ratio remained fairly constant at different Ca leaching efficiencies. It is necessary to assume all the leached barium will precipitate with CaCO$_3$ because the barium concentrations were reduced to below detection limits (0.05 ppm Ba$^{2+}$) after the precipitation step (Appendix B).

Although the barium phase in the waste concrete fines could have been acid-soluble, the solubility of Ba$^{2+}$ could be controlled by the solubility of a less soluble salt, such as BaSO$_4$, where sulphate was leached from other phases.

\[
\text{CaSO}_4(aq) + \text{BaCl}_2(aq) \leftrightarrow \text{CaCl}_2(aq) + \text{BaSO}_4(s)
\]

\[
K_{sp} \text{CaSO}_4 = 9.1 \times 10^{-6}, K_{sp} \text{BaSO}_4 = 1.1 \times 10^{-10}
\]

Based on a simplified model that the concentration of Ba$^{2+} = \sqrt{1.1 \times 10^{-10}}$ an equilibrium concentration of 1.44 ppm Ba in solution can be calculated, and the concentrations measured in the leaching experiments ranged from 1.10-3.00 ppm Ba in solution (Appendix B). This would support the hypothesis that the barium leaching is controlled by the solubility of BaSO$_4$, however after factoring the measured S concentrations (estimated as 0.008 M SO$_4^{2-}$) and the activity coefficients, the calculated BaSO$_4$ solubility is only 0.017 ppm Ba$^{2+}$:

\[
[\text{Ba}^{2+}] = \frac{k_{sp} \gamma}{\gamma[SO_4^{2-}] \cdot \gamma}
\]

where $\gamma \approx 0.33$ for Ba$^{2+}$ and SO$_4^{2-}$ when $I = 0.75$ M (Appendix G)

\[
[\text{Ba}^{2+}] = 1.26 \times 10^{-7} M = 0.017 \frac{mg}{L} = 0.017 \text{ ppm}
\]
Therefore BaSO$_4$ could have been supersaturated, or the dissolved sulphur might not have been predominantly present as sulphate. Measures to control the barium content of the CaCO$_3$ to lower levels can be included in future work, given that it is consistently a significant component of Portland cement (280 ppm Ba on average) (Lea, 1998).

### 4.2.3 Purity

Based on the results of the waste concrete leaching experiments and the chemical analysis of conventional CaCO$_3$ products (PCC and GCC), a comparison between the purity of the two can be made with respect to metal content (Figure 4.5). The results are compared to PCC that is composed of 98.5% CaCO$_3$, 0.6% MgCO$_3$, 0.1% Fe$_2$O$_3$ and 0.1% Al$_2$O$_3$; and GCC that contains 96.62% CaCO$_3$ and 2.43% MgCO$_3$ (similar to the chemical analyses of PCC and GCC listed by Casey (1983)). Figure 4.5 suggests that the iron and aluminum content of waste concrete PCC would be similar to that of conventional PCC when the solution pH is approximately 7.0, and the purity (with respect to these metals) can be improved by several orders of magnitude in more alkaline solutions. The magnesium content of the solutions are significantly greater than that of PCC and GCC when the pH is below ~10.4, however at pH 11.0 the magnesium content in solution can be significantly lower than in conventional PCC. Although this can provide some grounds for comparison, it should be noted that the particle size, brightness, surface area, and abrasiveness of CaCO$_3$ products appear to be more relevant properties to users.
Figure 4.5: Purity of calcium leaching solutions, represented by molar ratios of calcium to impurities, vs. pH compared to the ratios for conventional PCC and GCC.

4.2.4 Trace Element Leaching and Residual Fines

One concern with this process is that the leaching step changes the waste concrete from inert fill to a more hazardous waste due to enhanced trace element leaching. This was found with the use of steelmaking slags for mineral sequestration where vanadium and chromium were particularly more soluble in the residual slag, making it more hazardous than the original unprocessed slag (Eloneva et al. 2010-b).

Water-solubility tests were not conducted on the residual waste concrete fines in these experiments, however the solubility of trace elements during the calcium leaching experiments with 0.5 M HCl can still be assessed. The concentration of lead and chromium vs. pH after 2 hours of leaching are shown in Figure 4.6, these elements were selected because they are a common concern with waste concrete disposal (CSI, 2009). For reference, the lead and chromium leaching limit for inert waste at landfill taken from ALS Environmental (2016) is shown. It should be noted that the leaching tests for landfill waste classification use water as a solvent and use a liquid to solid ratio (L/S) of 10 L/kg, while the leaching experiments in this thesis used 0.5 M HCl and the L/S varied from 5-20 L/kg.
Figure 4.6: Co-leaching of trace elements from waste concrete fines by HCl during Ca-leaching vs. the pH of the solution after 2-hours of mixing. Leaching limits were taken from ALS Environmental (2016).

Figure 4.6 suggests that waste concrete materials are unlikely to be classified as a hazardous waste at landfill based on chromium and lead leaching as long as the pore water pH is between approximately 4.0-11.0, however future work should verify this under the appropriate leaching conditions with the leaching residues (Eloneva et al. 2010-b). The enhanced solubility of chromium (possibly Cr$^{6+}$) in more alkaline solutions could be due to hydrolyzation, which is typical of highly charged ($\geq$3) metal ions in non-acidic waters (White, 2013). Also of note is that the incorporation of chromium in the PCC can controlled by pH, no chromium was detected (Cr $<0.04$ mg/kg) the after the purification step at pH 9.0 (Appendix B). The amount of lead that was leached was below detection limits (0.03 mg/kg) when the pH was not acidic, and that which was leached in acidic solutions was also removed by the purification step.

The solubility of trace elements in the residual products is important from both an environmental and economic perspective. This can be see in Figure 4.7 where the mass of the residues (residual fines and purification residue) is shown relative to the mass of the product (PCC). The three clusters represent where three different volumes of 0.5 M HCl, the HCl:(Ca+Mg) ratio varied slightly within each cluster due to material differences. The results
show that with a low calcium extraction efficiency approximately 8.5 tonnes of residue was produced per tonne of PCC, however the relative amount of residue decreased to approximately one tonne of residue per tonne of PCC with full calcium extraction.

Figure 4.7: The mass of the dried residues relative the amount of product (PCC) that was produced.

In the worst case scenario the residual products would be treated as hazardous waste, and the disposal costs in Canada would be $65 CAN per tonne plus haulage (reviewed in Lafarge, 2014), and therefore cost between ~$550 per tonne of product with selective leaching (low HCl:(Ca+Mg) ratios), and ~$65 per tonne with full calcium extraction. However, it is possible that the fines produced by selective leaching would be less hazardous than those produced via full calcium extraction because the calcium left in the residue could act as a pH buffer against acid generated via the oxidation of ferrous iron in the residue. In fact, the acid neutralization capacity is a parameter that is assessed for when classifying waste for landfill (ALS Environmental, 2016). If deemed suitable, the residue would ideally be mixed back into the coarser recycled waste concrete materials at the recycling facility for use as road base.

4.3 Purification

In order to produce a value-added PCC product from waste concrete, it is important to remove iron and manganese from solution before the precipitation step as these metals strongly discolor the product. This purification step is not required when approximately 25% of the
calcium is targeted, as virtually no impurities leach out at this HCl:(Ca+Mg) ratio (~0.5), see Figure 4.4. It becomes necessary, however, at higher extraction levels that allow for more CO₂ to be sequestered per tonne of waste concrete. Another advantage of high calcium extraction efficiencies is that the less reactive minerals are carbonated (i.e. those less likely to passively carbonation through exposure to the atmosphere). The Ca(OH)₂ in cement is considered reactive, while the calcium silicates are considered less reactive. In order to remove iron and manganese, Ca(OH)₂ was added to raise the pH of the solution to 8.95±0.05. This pH was used for purification because with it no iron or manganese was detected in the PCC when analyzed by EDAX, and in order to keep the precipitation of Ca and Mg-silicates during purification to a minimum. Calcium and magnesium both produce a bright and relatively non-abrasive carbonate product.

4.3.1 Metal Precipitation

The concentration of calcium and magnesium was not dramatically altered by purification to pH ~9.0 (Figure 4.8). However, the concentration of calcium did actually decrease in most cases through the purification step, even though Ca(OH)₂(s) was added (Appendix B); the removal of calcium was up to 8.6% relative to calcium levels before purification. This is likely explained by the leaching of silica, and the precipitation of calcium-silicate at pH ~9.0. The calcium concentration increased significantly (~25%) via purification when the HCl:(Ca+Mg) ratio exceeded 2.0 because there was excess HCl that was neutralized by Ca(OH)₂. The calcium concentration increased slightly via the purification step when a high percentage of the calcium was dissolved from the high carbonate concrete (HCC), this is likely because the materials contained fewer calcium-silicates, meaning less silica was leached and therefore less was available to re-precipitate with calcium in the purification step. More Ca-silicate precipitation can be expected at a higher purification pH because the activity of dissolved silica begins to increase exponentially as the pH exceeds 9.0 (Figure 2.4).
Minor amounts of Mg were also precipitated, also likely as silicates based on Figure 4.12 and because at pH 9.0 Mg(OH)$_2$ is not expected to precipitate (Figure 2.6). The amount of Ca(OH)$_2$ added for purification is shown as how much Ca was added as Ca(OH)$_2$ relative to the amount of Ca in the feed materials (waste concrete fines). When 100% of the calcium was leached by the stoichiometric amount of HCl, the quantity of calcium added as Ca(OH)$_2$ for purification was less than 5%, and decreased to approximately 1% when around 60% of the calcium was leached (Figure 4.8).

![Figure 4.8: Leaching of calcium and magnesium from various waste concrete fines, and their content after Fe and Mn removal at pH ~9.0 by Ca(OH)$_2$ addition.](image)

At pH ~9.0, iron was removed to below detection limits (<0.05 µg/g solution) in most cases. Manganese was significantly reduced at this pH, but still detectable by ICP-OES (Figure 4.9).
Figure 4.9: Leaching of Fe and Mn from waste concrete fines and their removal at pH ~9.0.

The highest measured concentration of manganese after purification was 2.6 µg/g solution, with a total calcium and magnesium concentration of 10,207 µg/g solution. To make a conservative estimate of how much manganese could be incorporated into the PCC, it is assumed that only the manganese (2.6 µg/g solution) and calcium (9520 µg/g solution) precipitate as carbonates:

\[
\frac{2.6 \mu g \ Mn}{9520 \mu g \ Ca} \times \frac{1 \ mg \ Mn}{10^3 \mu g} \times \frac{40 \mu g \ Ca}{100 \mu g \ CaCO_3} \times \frac{10^9 \mu g}{1 \ kg} = \frac{109 \ mg \ Mn}{1 \ kg \ CaCO_3} = 109 \ ppm
\]

Thus, it is estimated that with a purification pH of ~9.0 the maximum expected concentration of manganese in PCC would be 109 ppm. For comparison, Belcher et al. (1983) found the manganese concentration in commercial PCC to be 0.2-0.6 ppm. Therefore the Mn concentration at pH ~9.0 is likely too high for PCC production, however Mn could easily be removed to below detection limits at a slightly higher pH. The results of the leaching experiments showed that when the solution pH was 9.34 the concentration of manganese was below detection limits (0.05 µg/g solution). Aluminum was removed to below detection limits.
(1.0 µg/g solution) in every case by purification to pH ~9.0. The highest zinc concentration measured after purification was 0.0390 µg/g solution, which is likely of no significance.

4.3.2 Purification Residues

4.3.2.1 Analysis

The mass of the purification residues relative to the amount of product (PCC) that was produced is also shown in Figure 4.10; with a purification pH of ~9.0 the mass is, at most, ~10%, unless HCl is added in excess. Silicate precipitation is suggested by the EDAX and thermal analyses of the purification residues that were produced when the HCl:(Ca+Mg) ratios was ≥ 1.6 (Figure 4.10 and Figure 4.11). This is because hydroxides and carbonates of calcium and magnesium were not identified in these residues (Figure 4.11), and Ca, Mg and Si were significant components of the waste (Figure 4.10). The mass loss observed in the TGA curve of the purification waste is likely H₂O loss, either hydrated or adsorbed. The TGAs of the two purification residues that were produced from when the HCl:(Ca+Mg) ratio was below 1.6 identified CaCO₃, likely due to slower dissolution kinetics of the added Ca(OH)₂, and its subsequent carbonation prior to analysis. In some of the residues trace amounts of sulphur were detected, this could be explained by the common ion effect from Ca(OH)₂ addition, inducing the precipitation of gypsum (CaSO₄·2H₂O). Purification residues were analyzed by XRD, and appeared to be amorphous (Appendix I).
Figure 4.10: EDAX results of the purification residues (left). The mass of the purification residues relative to the amount of product (PCC) that was produced (right). The purification pH was ~9.0. The EDAX analysis assumes only the measured elements are present, however hydrogen from H₂O content might be significant.

Figure 4.11: Thermal analysis of the purification residues.

4.3.2.2 Applications

Ideally, the purification residue could be recycled as cement kiln feed as it contains all of the primary ingredients for clinker (Si, Fe, Al, and Ca). However, this might be prevented by the presence of chloride. The chloride content of cement kiln feed is constrained because it causes corrosion on the steel reinforcements in concrete; the chloride content of aggregate used in
concrete is also constrained to 0.05% (reviewed in Tam et al., 2007). Therefore ensuring the residue is thoroughly washed is very important when a chloride solvent is used.

From the perspective of the life cycle CO\(_2\) balance, the emission produced from calcium in the residue (CaCO\(_3\) → Ca-silicate + CO\(_2\)) could be cancelled if the residue can be used as cement kiln feed because it would displace the calcination of new CaCO\(_3\).

The presence of magnesium might be a deterrent for the residue’s acceptance as cement kiln feed because the upper limit for magnesium in clinker (the product of a cement kiln) is typically 1.8% Mg (reviewed in Oates, 1998, p.82). The limit on Mg content exists because it persists as MgO, and higher MgO contents lead to long-term unsoundness of structures; this arises from very slow hydration, accompanied by expansion, of free MgO (periclase) crystals (Lea, 1998, p. 176). The Mg content of the residue is determined by the amount leached and the purification pH, where more Mg can be expected at a higher purification pH. The Mg:Fe wt% ratio in the purification residues varied between 1.0 and 2.5 when the HCl:(Ca+Mg) ratio was between 1.6 and 2.0 when the purification pH was ~9.0 (see Figure 4.10). This might mean the purification residue is unacceptable as a stand-alone iron source for cement kiln feed because the Mg:Fe wt% ratio in Portland cement is 0.5 on average (Lea, 1998, p. 137). The Mg:Al wt% ratios in the purification residues (1.8 to 2.7) are also significantly greater than that of Portland cement (0.37). When an excess of HCl was added and more Fe and Al was dissolved (Figure 4.4) the Mg:Fe and Mg:Al ratios in the purification are likely acceptable for reuse as cement kiln feed (0.66 and 0.16, respectively). However, since the magnesium in the purification resides appears to be in silicate form, it may not cause the same issues as MgO, the residue might also be blended in as minor component.
4.4 Precipitation

4.4.1 Precipitation Efficiency

The calcium-rich solutions were mixed with an equal volume of Na$_2$CO$_3$(aq) that had a concentration of 0.25 M, i.e. half that of the HCl used for leaching, resulting in approximately equivalent moles of Ca(+Mg) and CO$_3$. The calcium precipitation efficiency was consistently greater than 99.9%. Precipitation efficiencies were calculated based on the measured values (ICP-OES data in Appendix B) before and after precipitation.

The leaching of Na and K from waste concrete by HCl could have influenced the precipitation efficiency of calcium by creating a slight excess of CO$_3^{2-}$ relative to calcium, where an excess of CO$_3^{2-}$ will influence the solubility of CaCO$_3$ through the common ion effect. The leaching efficiency of sodium and potassium increased as the HCl:(Ca+Mg) increased (Appendix I), this suggests that these elements were actively leached by HCl, rather than through the dissolution of NaCl and KCl.

While the calcium precipitation efficiency was consistently over 99.9%, that of magnesium was less due to greater solubility of MgCO$_3$. The combined precipitation efficiency of Ca+Mg was on average 98.1%, and ranged from 99.9% to 93.4%.

4.4.2 Purification Requirements for Electro dialysis

After the precipitation step, a solution of NaCl remains, and from this solution, NaOH and HCl can be regenerated via membrane-based electrochemical methods. However, the NaCl solution should ideally contain less than 2 mg/L of calcium, less than 1 mg/L of magnesium, and less than 5 g/L sulphate after primary purification (Ullmann’s, 1996). Calcium and magnesium should be removed to these levels in order to avoid membrane fouling via the precipitation of hydroxides, and the sulphate is removed to avoid steel corrosion (IPPC, 2001).
From Figure 4.12 it can be seen that the sulphate concentration (calculated assuming all
the sulphur was in sulphate and a solution density of 1 g/mL) was consistently below the limit of 5
g/L; the average concentration was 0.46 g/L and is likely a result of the high calcium levels
controlling sulphate levels via gypsum solubility in the steps before CaCO$_3$ precipitation. The
calcium levels after precipitation were also consistent, with an average concentration of 3.2 mg/L;
this is slightly above the ideal limit of 2 mg/L. The magnesium levels varied from 105 mg/L to
less than 0.5 mg/L. The concentration was below the limit of 1 mg/L in some cases because
sufficiently low magnesium was present before precipitation (Appendix B). Magnesium can be
removed as Mg(OH)$_2$ by adding NaOH. Future work should determine if silica and carbonate also
need to be removed in order to avoid the accumulation of silica-gel on the membrane surface and
the outgassing of CO$_2$ in the acidic chamber of the cell.

![Figure 4.12: The log concentration of Ca (mg/L), Mg (mg/L) and SO$_4$ (g/L) in solution after precipitation vs. pH.](image)

4.4.3 Physical Characteristics of Product

When the HCl:(Ca+Mg) ratio was approximately 0.5 and the solution pH was more
alkaline before Na$_2$CO$_3$ addition, the precipitate consisted of rhombohedral calcite and
polycrystalline vaterite spheres (a metastable polymorph) after 30 minutes of mixing, and the
particles were approximately 6 µm in diameter (Figure 4.14 and Appendix D). The presence of
metastable vaterite was likely due to the relatively short reaction time of 30 min, which was used because Gao et al. (2007) had shown significantly larger particles were produced with longer reaction times (≥60 min). Changes in the Ca$^{2+}$/CO$_3^{2-}$ ratio throughout the course of precipitation might also explain the presence of vaterite because it has been shown to form at lower Ca$^{2+}$/CO$_3^{2-}$ levels (Meldrum and Colfen, 2008). The vaterite-calcite transition was found to take place after the precipitate was put back into deionized water and was mixed for an additional 24 hours at 400 rpm. Although the CaCO$_3$ morphology was uniform, the size of the particles was significantly larger than 2.0 µm. The approximate size used for paper making applications is 2.0 µm (Teir et al., 2005).

The size and shape of the particles was dramatically changed when the HCl:(Ca+Mg) ratio was increased to 2.0 and the solutions were purified to pH 9.0 before Na$_2$CO$_3$ addition. The particles had an elongated shape and the particle size was reduced to ~2 µm in length. The particles also appear to be relatively stable because no significant changes were observed by XRD or SEM between 30 minutes and 24 hours of reaction time (Appendix D and I). XRD identified the only crystalline phase to be magnesian calcite, and likely an amorphous phase at both time steps. It is difficult to interpret if the observed changes were due to the incorporation of magnesium, the influence of silica (Kellermeier et al., 2013) that was leached at higher HCl:(Ca+Mg) ratios, or other factors. The PCC in Figure 4.14 was analyzed by EDAX and was found to contain only the appropriate elements for magnesian calcite, with the exception of a trace amount of sodium (Appendix I).
Figure 4.13: SEM images of PCC produced with a HCl:(Ca+Mg) ratio of 0.5 with 30 minutes of reaction time after Na$_2$CO$_3$ addition (top two) and after an additional 24 hours of reaction time in deionized water (bottom two).

Figure 4.14: SEM images of PCC produced with a HCl:(Ca+Mg) ratio of 2.0 and a purification pH of 9.0.
The morphology of PCC was also studied at higher purification pH values were also studied when 100% of the calcium was targeted from the low carbonate concrete materials with a HCl:(Ca+Mg) ratio of 2.0. The pH was adjusted to 10.0, 11.0 and 12.0 via the addition of 1.0 M NaOH. The SEM results showed that after 30 minutes of reaction time the smaller elongated magnesian calcite particles were still produced with pH 10.0, the rhombodehral calcite and vaterite spheres were produced at pH 11.0, and only rhombohedral calcite was produced at pH 12.0 (Figure 4.15).

![Figure 4.15: SEM images of PCC produced from low carbonate concrete with a HCl:(Ca+Mg) ratio of 2.0 at various purification pH values (10.0, 11.0 and 12.0 from left to right).](image)

The purification residues were also analyzed by EDAX and the mass of the residue was measured, this allowed for the precipitation of calcium, magnesium in the residue to be estimated (Appendix I). The incorporation of calcium in the purification residue increased moderately between pH 9.0 and 11.0, and greatly between 11.0 and 12.0. The amount of magnesium incorporated into the PCC was significantly reduced after purification to pH 11.0.

### 4.4.4 Comparison with TGA Results

The amount of PCC produced can be verified using two methods (Figure 4.16). Firstly, amount of PCC produced can be evaluated with the difference in Ca + Mg concentrations in solution before and after precipitation (ICP-OES), and through TGA analysis of the precipitate. The first tabulates the moles of Ca+Mg precipitated while the second calculates the moles of CO₂ released from the precipitate. In the TGA analysis, the mass loss between 300-800°C was interpreted to be due to the sublimation of CO₂ from MgCO₃ and CaCO₃.
Figure 4.16: Comparison of two different methods, measuring the amount of CO$_2$ precipitated as carbonates by TGA, and the amount of Ca+Mg precipitated by ICP-OES.

From Figure 4.16 it can be seen that the ICP-OES values are consistently greater than that calculated by TGA, and the difference between the two methods increases with increasing Ca+Mg precipitation (i.e. higher HCl:(Ca+Mg) ratios). It is likely that the TGA method underestimates the amount of Ca+Mg precipitated for two main reasons. The first and most likely reason is that some PCC is retained by the filter paper, and its mass was not included in the calculations. The second reason is that the TGA does not detect Ca or Mg that is associated with silicates, and trace amounts of silicates could have precipitated if there was residual silica in the solution before the carbonate precipitation step.

### 4.5 Preliminary Process Analysis

The objective of this work is to provide a sustainable method for recycling waste concrete. As such, it is important to estimate the energy consumption of the proposed process and compare it to existing technologies.
4.5.1 Comminution

In this study, waste concrete boulders (Dp≈25cm) were crushed via jaw crusher and the finest two size fractions were recovered for the leaching experiments; the results showed that between 8.3% and 9.0% of the mass of the original concrete can be recovered in these two fractions (Table 4.1). While similar fraction could be recovered from existing concrete recycling facilities, the energy requirements for crushing are still estimated using the particle size distribution plot and Bond’s Equation (Equation 2.1):

$$E = 10W_i\left(\frac{1}{\sqrt{F_{80}}} - \frac{1}{\sqrt{F_{80}'}}\right)$$

The chemical composition of the two size fractions and the recovered masses can be included to determine the energy required for crushing per tonne of CaCO₃ produced. Finally, the energy requirements for the crushing step in the context of PCC production can be assessed as a function of the calcium extraction efficiency.

Figure 4.17: The particle size distribution of two crushed waste concrete samples.

The particle size distribution in Figure 4.17 shows the cumulative mass percentage of particles that have a diameter below a particular size. The high carbonate concrete and low carbonate showed similar results when crushed with the same method. Bond’s equation
(Equation 2.1) requires the 80% passing size of the product ($P_{80}$) to be known; this was calculated to be 6,980 µm. The 80% passing size of the feed ($F_{80}$) is estimated to be 500,000 µm (50 cm).

For the high carbonate concrete the Bond’s work index of limestone (11.7) was used because the primary aggregate type was dolomitized limestone. The low carbonate concrete contained more gneiss, syenite, and quartzite gravel aggregate compared to dolomitized limestone (as determined by visual inspection and TGA), and the work index was estimated to be 17.0 (similar to quartzite).

The fines will require transportation from the grinding site to the leaching facility. It is assumed this will be accomplished mechanically (e.g. conveyor belt) and require a negligible amount of energy.

| Table 4.5: Calculation of Comminution Energy per tonne PCC produced. |
|--------------------------------------------------------------|-----------------|-----------------|
| Wi (kWh/tonne) | 11.7 | 17.0 |
| E (kWh/tonne concrete) | 0.877 | 1.28 |
| kg Ca in fines (Dp<425 µm) / tonne concrete | 15.2 | 12.8 |
| kWh/tonne Ca recovered | 58 | 100 |
| kWh/ tonne CaCO$_3$ | 23.2 | 40.0 |

Of note in the calculation above is that the hardness, or work index ($W_i$), of the waste concrete, here estimated based on aggregate type, has a significant effect on energy demand. Specifically, a 20% reduction is Ca content is paired with a 70% increase in unit energy consumption. This level of energy penalty is associated with 100% recovery of Ca from the

\[
\frac{kg \text{ Ca in } Dp<425 \mu m \text{ fraction}}{\text{tonne concrete}} = (\text{wt}\% \text{ fine} \times \% \text{Ca fine}) + (\text{wt}\% \text{ coarse} \times \% \text{Ca coarse}); \text{ values taken from Tables 4.1 and 4.2}
\]

98
waste. Lower recovery efficiencies will lead to higher unit energy consumption, as shown below in Figure 4.19.

![Figure 4.18: The energy required for crushing to produce one tonne of CaCO\(_3\) from the waste concrete fines (Dp<425 \(\mu\)m) as a function of the calcium extraction efficiency.]

4.5.2 Mixing

The model of a continuously stirred reactor (CSR) is a suitable industrial equivalent to what was used in the leaching experiments for mixing. However, other mixing methods are possible such as a fluidized bed (where gas bubbles can be used to suspend and mix particles), or a fixed bed of solids with liquids circulating via pumping. To estimate the amount of energy required for the CSR, mixing equations from Nagata (1975) can be used, as was done by Kakizawa et al. (2001). The total power (P) is calculated based on the fluid properties (\(N_p\)), density (\(\rho\)), mixing speed (n) and propeller length (d).

\[
P = N_p \rho n^3 d^5 \quad (4.6)
\]

\[
N_p = \frac{A}{Re} + B \left( \frac{1000 + 1.2 Re^{0.66}}{1000 + 3.2 Re^{0.66}} \right) + \left( \frac{Z}{D} \right)^{0.35} + \frac{b}{D} (\sin\theta)^{1/2} \quad (4.7)
\]

\[
A = 14 + \left( \frac{b}{D} \right) \left[ 670 \left( \frac{d}{D} - 0.6 \right)^2 + 185 \right] \quad (4.8)
\]

\[
B = 10 \left[ 1.3 - 4 \left( \frac{b}{D} - 0.15 \right)^2 - 1.14 \left( \frac{d}{D} \right) \right] \quad (4.9)
\]

\[
P = 1.1 + 4 \left( \frac{b}{D} \right) - 2.5 \left( \frac{d}{D} - 0.5 \right)^2 - 7 \left( \frac{b}{D} \right)^4 \quad (4.10)
\]

\[
Re = \frac{na^2 \rho}{\mu} \quad (4.11)
\]
<table>
<thead>
<tr>
<th>Power Consumption</th>
<th>D [m]</th>
<th>Z [m]</th>
<th>d [m]</th>
<th>b [m]</th>
<th>θ [°]</th>
<th>ρ [kg/m³]</th>
<th>n [s⁻¹]</th>
<th>µ [Pa·s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tank diameter</td>
<td>Tank height</td>
<td>Propeller length</td>
<td>Propeller thickness</td>
<td>Propeller angle</td>
<td>Fluid density</td>
<td>Stirring speed</td>
<td>Fluid viscosity</td>
<td></td>
</tr>
</tbody>
</table>

The shape of the tank reactor is assumed to be a cylinder with a diameter (D) equal to its height (Z), and that the propeller length (d) is D/2, with a thickness (b) of D/10. The fluid properties (ρ and µ) are estimated to be equal to those of pure water (1000 kg/m³ and 0.001 Pa·s). From Equation 4.6 it can be seen that the power requirements for mixing increasing rapidly as the size of the tank increases, 5 m³ tanks are assumed in the calculation. A stir speed of 400 rpm (6.7 rps) is used in the power calculation as this was used in the leaching experiments because it was found to be the minimum speed to suspend all of the particles. With these conditions and Equation 4.6-4.11 it was calculated that stirring a 5 m³ tank requires 91 kW/m³. A CaCl₂ concentration of 0.25 M is used convert this mixing power to 3,640 kW/tonne CaCO₃.

Alternatively, the fluid can be circulated via pumps through the fixed bed of solids. Here the pump circulates 20 m³ of solution in a 5 m³ reaction vessel over the 2h reaction period. The energy penalty is associated with the gravitational potential energy (mgh), where the height can be set arbitrarily at 2 m above the reaction vessel. The energy required to cycle 20 m³ (20,000 L) of solution is 392 kJ or 0.12 kWh at 90% pump efficiency. This translates to 0.24 kWh per tonne of CaCO₃ with a 0.25 M CaCl₂ solution. This value is assumed for the energy consumption due to mixing, and since it is negligible, it is omitted. Further experimental study is necessary to study alternative mixing methods.

4.5.3 Production of Na₂CO₃ from gaseous CO₂ source

NaOH can be readily converted to Na₂CO₃ through contact with a CO₂ bearing gas. The entire cost of capturing CO₂ from the atmosphere with NaOH has been estimated at $91/tCO₂ or $36.4/t CaCO₃ (Zeman 2014). The energy penalty associated with this technology is 480 kWh/t CO₂ or 192 kWh/t CaCO₃.
4.5.4 Purification Agents

Calcium hydroxide was used to purify the solutions, and to estimate the energy requirements for its production the values that were reported by Teir et al. (2005) for conventional PCC production were used since they both involve the calcination of limestone. The CO$_2$ liberated from CaCO$_3$ during calcination is excluded because the purification waste was analyzed by TGA, and the results suggested any unreacted Ca(OH)$_2$ will readily re-absorb CO$_2$ when exposed to air (Figure 4.11). Any Ca(OH)$_2$ that remains in solution after purification is re-carbonated through reaction with Na$_2$CO$_3$. It is acknowledged that some of the Ca(OH)$_2$ was likely converted to calcium silicates during the purification reaction, however this amount is excluded from the analysis because it is assumed that the purification waste could be tailored for reuse as cement kiln feed. Therefore Ca(OH)$_2$ production is assumed to require 840 kWh/tonne Ca(OH)$_2$ and produce 283 kg CO$_2$/tonne Ca(OH)$_2$ due to the combustion of heavy fuel oil$^{29}$. 

4.5.5 Solid-liquid Separation

Kodama et al. (2008) reviewed that existing solid-liquid separation equipment had a solid separation capacity of 14 tonnes per hour and a power consumption of 76 kW; therefore it is assumed that all filtration steps require 5.4 kWh per tonne of solids separated. With this the total energy required to filter the residual fines, purification waste and CaCO$_3$ per tonne of CaCO$_3$ recovered can be estimated. Differences in the filterability of the residual fines (i.e. the extent of silica gel formation) at higher calcium extraction efficiencies are not considered. Since multiple cycles of rinsing could be required to sufficiently remove NaCl, the value of 5.4 kWh/t is tripled to 16.2 kWh/t of solids. With this value and the measured masses of product (PCC), residual fines, and purification that were produced at different HCl:(Ca+Mg) ratios (Figure 4.20), the energy requirements for filtration per tonne of PCC can be estimated (Table 4.6).

---

$^{28}$ Converted from 2,244 MJ/tonne CaCO$_3$ reported by Teir et al., (2005).
$^{29}$ Converted from 210 kg CO$_2$ from heavy fuel oil per tonne CaCO$_3$ (Teir et al., 2005).
Table 4.6: The Specific Energy Consumption of the Filtration Step with Two Additional Filtration Cycles for Rinsing.

<table>
<thead>
<tr>
<th>HCl/(Ca+Mg)</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>kWh/tonne PCC</td>
<td>150</td>
<td>75</td>
<td>37.5</td>
</tr>
</tbody>
</table>

4.5.6 Acid and Alkali Regeneration

In order to create a closed loop system, the NaCl produced during precipitation must be converted to HCl and NaOH. Solutions of 0.5 M HCl were used in the leaching experiments in this study primarily because Carmen (1993) showed that relatively low concentrations of HCl and NaOH require less energy to be produced via BMED. From the literature this chemical regeneration step was found to require significantly more energy than other process steps, and therefore the concentration of chemicals was tailored to it.

From the reviewed literature, the regeneration of HCl and NaOH through bipolar membrane electrodialysis (BMED) consumes less energy per unit product than regeneration through membrane electrolysis (the chlor-alkali process). In addition, BMED does not produce chlorine gas, has a lower capital cost, and can operate using dilute salt solutions. BMED systems are considered a viable method to regenerate chemicals from the salts of industrial effluents (Ghyselbrecht et al., 2014).

Since acid and alkali recovery was not part of the experimental program, the energy requirements can only be estimated from the results of previous authors. None of the reviewed studies on BMED estimated the energy required to regenerate HCl and NaOH from 0.25 M NaCl; however in a recent study Shuto et al. (2015) recovered HCl and NaOH from a 2.5 M NaCl solution. They found the chemicals could be regenerated for ~375 kJ/mole with a 55% NaCl recovery, and for ~250 kJ/mole with a 35% NaCl recovery. This means that 3,160 kWh - 4,730 kWh would be required to capture one tonne of CO₂, or 1,390 kWh - 2,080 kWh per tonne CaCO₃. More dilute NaCl solutions were not tested, however an earlier study by Shuto et al. (2014) found that more dilute solutions of NaNO₃ led to a higher recovery ratio for an equal
amount of energy input. Alternatively, Carmen (1993) used a saturated NaCl brine, and found a 1.0 M acid and alkali pair could be produced for 1,358 kWh/tonne CaCO$_3$. A value of 1,390 kWh/tonne CaCO$_3$ will be used to estimate the energy requirement as it best represents the case of regenerating relatively dilute chemicals from an unsaturated NaCl solution.

4.5.7 Transportation

If CO$_2$ is sourced from the atmosphere through absorption by NaOH at the waste concrete recycling facility, then the transportation of waste concrete fines and/or compressed CO$_2$ to the PCC production site is not required. However, the residual fines and PCC will still need to be transported. It is assumed that both sites are 100 km away from the production site, and that 40 tonnes trucks travel there fully loaded, and return to site empty. Eloneva et al. (2012) reviewed that the CO$_2$ emissions from a full trailer load (40 tonnes) are 1.335 kg CO$_2$ per km and 0.879 kg CO$_2$ per km when empty. Therefore, the emissions from transportation are estimated to be 221.4 kg CO$_2$ per 100 km between sites (200 km round trip) per 40 tonnes of cargo. The results of the experiments with LCC fines suggested that approximately 460 kg of PCC and 500 kg of residual fines are produced per tonne of fines when the HCl:(Ca+Mg) ratio is equal to 2.0. It was then calculated that approximately 11.5 kg of CO$_2$ are produced per tonne of PCC by transporting the PCC and residual fines to sites that are both 100 km away (Figure 4.19).

Figure 4.19: Emissions from transportation if PCC is produced at the waste concrete recycling facility, and the paper mill and residue disposal site are both 100 km away.
A transportation sensitivity analysis is shown in Figure 4.20, where the transportation emissions and costs are shown as a function of the distance between sites for various calcium extraction efficiencies. Transportation costs were estimated at $5 U.S. per tonne∙100 km from World Bank (2016). Higher calcium extraction efficiencies are more favourable because less residue needs to be transported offsite per tonne of PCC that is produced (Figure 4.21). The emissions from transportation are fairly minimal compared to the CO₂ sequestration capacity of PCC when the calcium extraction efficiency is at least 50% and the products are transported to sites that are less than 100 km away. The transportation costs are more significant given that PCC is valued at $200-500 per tonne, however the costs are minimal for high calcium extraction efficiencies and distances below 100 km.

![Figure 4.20](image)

**Figure 4.20:** The emissions and costs associated with transporting PCC and residual products vs. the distance between sites for various calcium extraction efficiencies.

4.5.8 Material, Energy and CO₂ Balance

The mass flow of materials vs. the HCl:(Ca+Mg) ratio is shown in Figure 4.21, where both LCC and HCC starting materials were used. It is worth noting that although the LCC materials were carbonated (i.e. CO₂ was absorbed by the materials), the measured mass of the final solids was not significantly greater than that of the original waste concrete fines. The
expected mass increase in the final materials can be estimated based on carbonation of the CaO in the cement (primarily from $3\text{CaO}\cdot2\text{SiO}_2\cdot3\text{H}_2\text{O}$), where 44 g of CO$_2$ is absorbed for every 56 g of CaO in the starting material. Since ~70% of the calcium in the LCC materials was uncarbonated (CaO), and the materials consisted of ~17% total calcium by mass, it can be predicated the total mass of solids should increase by 13.1% after carbonation.$^{30}$ There are two main factors that explain why this increase in mass was not detected.

The first is that the original materials contained significant amounts of H$_2$O as moisture and in hydrated minerals (primarily $3\text{CaO}\cdot2\text{SiO}_2\cdot3\text{H}_2\text{O}$, Ca(OH)$_2$, and CaSO$_4\cdot2\text{H}_2\text{O}$). If it is estimated that the mass loss from the TGA of the LCC materials up to 450°C (the end of the Ca(OH)$_2$ dehydration curve) was all H$_2$O loss, then it can be estimated they contained ~7% H$_2$O (Figure 3.3). The TGA’s of the products and residues suggested they did not contain as significant levels of H$_2$O.

The second factor that could help explain the unaccounted mass increase relates to silicon leaching, which was not studied by the analytical method used in this thesis. However, it was studied by Shuto et al. (2014) who found that silicon leaching from waste cement increased with increasing calcium leaching efficiency, and that waste cement contained ~11% silicon by mass. Since the authors used particles with Dp below 212 µm, the majority of the silicon was likely associated with cement rather than quartz sand (SiO$_2$) due to separation by sieve. Silicon from quartz sand is unlikely to be leached by HCl and form a colloid. In this thesis the mass of silicon in the solutions could not be estimated based on the solubility of silica (Figure 2.4) due to the possibility of colloidal silica (Bao et al., 2010), and all of the leached silica may not have been removed in the purification step. The mass of silicon recovered in the purification residues accounted for approximately 1.5% of the mass of the original solids when the HCl:(Ca+Mg) ratio

\[ \frac{\text{mass uncarbonated Ca}}{\text{mass uncarbonated Ca}} \times \frac{56 \text{ g CaO}}{40 \text{ g Ca}} \times \frac{44 \text{ g CO}_2 \text{ added}}{56 \text{ g CaO}} = 13.09\% \text{ mass} \]
was approximately 2.0 (Figure 4.10 and Figure 4.20), this is significantly less than the silicon content of waste cement described by Shuto et al. (2014). Therefore the cumulative mass associated with H$_2$O content and silicon leaching could explain why the expected 13.1% mass increases was not detected. A significant mass change in the HCC materials is not expected due to their low uncarbonated calcium content, and therefore presumably also a low leachable silica content.

![Graph showing mass fraction of materials when various types of waste concrete fines (LCC and HCC) were dissolved by three different volumes of 0.5 M HCl. More product and less residues are produced at higher HCl:(Ca+Mg) ratios due to more efficient calcium leaching and utilization.](image)

The most promising conditions for CO$_2$ sequestration through PCC production are assessed in Table 4.7. This is where 100% of the calcium is dissolved from low carbonate waste concrete fines (Dp<425 μm) when the HCl:(Ca+Mg) ratio equals 2.0 and the PCC contains some magnesium. In the following calculations, a carbon intensity of 0.04 kg CO$_2$ per kWh for electricity is used as a representative value of carbon intensity for Ontario power generation in 2015 (CEI, 2015). Diesel was assumed to produce 0.27 kg of CO$_2$ per kWh. The emissions from Ca(OH)$_2$ production were from the fuel used, where 283 kg CO$_2$/tonne of Ca(OH)$_2$ is produced.
Table 4.7: Summary of material and energy balance for PCC Production where HCl:(Ca+Mg) = 2.0, purification pH = 9.0 and electricity generation produces 0.04 kg CO₂/kWh.

<table>
<thead>
<tr>
<th>Operation</th>
<th>kWh/t PCC</th>
<th>Percentage of Energy</th>
<th>Energy Source</th>
<th>kg CO₂ emitted/t PCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crushing</td>
<td>40</td>
<td>2.3%</td>
<td>Electricity</td>
<td>1.6</td>
</tr>
<tr>
<td>Filtration</td>
<td>37.5</td>
<td>2.2%</td>
<td>Electricity</td>
<td>1.5</td>
</tr>
<tr>
<td>NaOH + HCl Regeneration via BMED</td>
<td>1,390</td>
<td>80.5%</td>
<td>Electricity</td>
<td>55.6</td>
</tr>
<tr>
<td>Ca(OH)₂ for Purification</td>
<td>25.2</td>
<td>1.5%</td>
<td>Heavy Fuel Oil</td>
<td>8.5</td>
</tr>
<tr>
<td>CO₂ Capture (1,110t air/t PCC)</td>
<td>192</td>
<td>11.0%</td>
<td>Electricity</td>
<td>7.7</td>
</tr>
<tr>
<td>Transportation</td>
<td>43</td>
<td>2.5%</td>
<td>Diesel</td>
<td>11.5</td>
</tr>
<tr>
<td>Total</td>
<td>1,727.7</td>
<td>100%</td>
<td>-</td>
<td>86.4</td>
</tr>
</tbody>
</table>

From Table 4.7 it can be seen that the total estimated energy demand for PCC production through the CO₂ capture process is 1,800 kWh/t PCC, and the process + transportation emissions are estimated at 90 kg CO₂/t PCC. By estimating that 70% of the leached calcium was initially uncarbonated (LCC, Table 4.2), approximately 300 kg of CO₂ are sequestered per tonne of PCC produced. Although the energy required for the main process step (BMED) is over twice that of the conventional method involving calcination (Table 2.2), the production of PCC from waste concrete as described in this thesis can sequester a net 210 kg CO₂/t PCC, rather than emitting 210 kg CO₂/t PCC. The net CO₂ balance is highly dependent on the carbon intensity of electricity, this relationship is illustrated in Figure 4.22.

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31 250 kJ/mole HCl/NaOH regenerated with ~35% NaCl recovery from a 2.5 M NaCl solution (Shuto et al., 2015)
32 0.03 tonnes Ca(OH)₂ per tonne PCC estimated from Figure 4.22 when HCl:(Ca+Mg)=2.0
33 Where air is 400 ppm CO₂, and PCC is 44% CO₂ by mass
The energy demand and emissions can also be evaluated for lower HCl:(Ca+Mg) ratios (Figure 4.23). From this it can be seen that the energy demand is only slightly less with higher extraction efficiencies, however a high extraction efficiency is associated with significantly less emissions because less waste needs to be transported per tonne of PCC produced.
The potential scale for CO₂ emission reductions with this method can be estimated from Table 4.1 and 4.2, where it can be calculated that 8.3% of the mass of the original concrete (LCC) was recovered as fines (Dp<425 µm), and that these fines contained 12.8 kg of calcium per tonne of concrete. Therefore 32 kg of CaCO₃ can be produced per tonne of waste concrete (LCC), and up to 9.9 kg of CO₂ can be sequestered per tonne of waste concrete. In 2009 it was reported that over 900 million tonnes of waste concrete were generated per year in the U.S., Europe and Japan combined (CSI, 2009). Therefore the current scale of this carbon capture method is estimated to be up to 8.9 million tonnes of CO₂ per year (28.8 million tonnes of CaCO₃) from the fine fraction (Dp<425 µm) alone. This is equivalent to taking 6.1 million cars off the road annually (EPA, 2014). However, it should be noted that these results are highly dependent on the characteristics of the waste concrete, the crushing methods, and the carbon intensity of electricity that is being used.

If 28.8 million tonnes of CaCO₃ can be produced from the fines (Dp<425 µm) per year with current waste concrete generation rates, then the fines should be sufficient to supply the global PCC demand of 14 million tonnes per year (Roskill, 2012). Replacing the conventional PCC production method would serve as helpful starting point for the development of this type of carbon capture technology, however, the scale could extend to ground calcium carbonate (60 million tonnes CaCO₃/year) if the efficiency of cement recovery from waste concrete was improved by also targeting the coarser fractions.

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34 Where ~70% of Ca was originally uncarbonated (LCC) and ~100% of calcium was dissolved and precipitated as CaCO₃
Chapter 5

Conclusions and Recommendations

The focus of this thesis was to investigate the possibility of sequestering CO$_2$ through the utilization of waste concrete as a source of uncarbonated calcium for CO$_2$ mineralization via CaCO$_3$ production. The uncarbonated calcium phases (predominantly calcium silicate hydrate and calcium hydroxide) are associated with the cement component of waste concrete. The experimental program focused on the recovery of cement from waste concrete, leaching up to 100% of the calcium, purifying calcium-rich solutions, and producing potentially marketable precipitated calcium carbonate (PCC) via Na$_2$CO$_3$ addition.

The primary use for PCC is in paper manufacturing, and should CO$_2$ be released from the PCC at any point during the life cycle of paper, CO$_2$ is still considered sequestered because CO$_2$ would otherwise be released from PCC made directly from virgin limestone. In other words, if CO$_2$ is released from PCC made via mineral carbonation the net emissions are considered zero, rather than positive if CO$_2$ is released from PCC made directly from virgin limestone. The global market for PCC could support the utilization of several million tonnes of CO$_2$ per year. Other markets for CaCO$_3$ made via cement carbonation include GCC and as a limestone replacement for cement production, however these are less valued products and are less likely to provide sufficient economic support for the process. If the market for PCC is met via cement carbonation, then the remaining supply of waste cement might be carbonated with less energy intensive methods (similar to Harrison, Power and Dipple (2012)) that do not produce potentially marketable CaCO$_3$.

The production of PCC via waste cement carbonation could promote broader sustainability because the inclusion of a waste cement recovery step into processes that produce recycled aggregates and sand from waste concrete could help create wider applications for them.
This is because removing the cement component from recycled aggregates and sand reduces their porosity, thus making them more suitable for use in new concrete (provided that they can be separated from porous leaching residues of clay and amorphous silica). The ultimate goal of zero waste within the concrete industry might be achieved through the combined production CaCO$_3$, recycled coarse aggregates, recycled sand, and the use of iron and aluminum rich residues as a clay substitute for cement kiln feed. The key sustainability benefits of zero waste are likely associated with minimizing the transportation of resources and waste to and from urban areas, resolving issues associated with public opposition to new aggregate quarries and land usage issues and fees for disposal.

Based on energy consumption, the process considered in this thesis is not competitive with other methods that utilize concentrated streams of CO$_2$ to produce PCC via cement carbonation (Kodama et al., 2008, Iizuka, 2006 and Kakizawa et al. 2001). These methods require less energy because concentrated CO$_2$ and is used to regenerate the leaching agent and also precipitate CaCO$_3$. Therefore the main point of merit to this process is that it can potentially be used with renewable energy sources and remove CO$_2$ from the atmosphere. The role of air capture is mainly to offset the emissions from small and mobile CO$_2$ sources such as transportation vehicles. Although sourcing CO$_2$ from the atmosphere for onsite PCC production could also minimize the costs and emissions associated with transporting raw materials, this is unlikely to be a significant advantage, at least in Toronto, Canada at the present time. This is because several gas-fired power plants (CO$_2$ sources) and waste concrete aggregate recycling facilities are located in close proximity to each other (Lafarge, 2014 and IESO, 2016).

If the energy consumption of BMED does not become more competitive through improvements in efficiency then an alternative process for PCC production though air capture could involve a combination of the caustization and calcination method to produce a concentrated stream of CO$_2$ via air capture (Keith et al., 2006 and Zeman, 2007) and the CO$_2$ pressure swing
method for PCC production through mineral carbonation (Iizuka, 2006). With this the combined energy consumption for calcination and CO$_2$ pressurization to 3.0 MPa can be estimated at 720 kWh/tonne CaCO$_3$ if a pure stream of CO$_2$ is recovered at atmospheric pressure from the lime kiln (Katsuyama et al., 2005, Teir et al., 2005 and Yamasaki et al., 2006).

### 5.1 Cement Recovery from Waste Concrete

The cement recovery step involved crushing waste concrete into aggregate sized particles (5 mm<Dp<10 mm) and recovering the fines (Dp<425 µm) by sieve for the leaching step. The cement recovery results were strongly influenced by the composition of the natural aggregates in the waste concrete. Up to 70% of calcium in the fines was associated with the cement phases when the concrete contained igneous and metamorphic aggregates. However, softer limestone and dolomite aggregates were significantly incorporated into the fines by crushing, and the fines were significantly less suitable for mineral carbonation.

This suggests that the geology of a region, in particular the aggregate source, plays an important role in the suitability of this process for CO$_2$ sequestration. In addition to aggregate composition, thinner concrete slabs of lesser compressive strength are also less likely to be suitable for mineral carbonation due to enhanced passive carbonation throughout the materials service life.

However, it should be noted that even without CO$_2$ sequestration through mineral carbonation, fugitive emissions can be avoided while also recycling waste materials with the chemical process considered in this thesis. This is because BMED utilizes electrical energy and the conventional PCC manufacturing process requires thermal energy, meaning that low carbon electricity can be used instead of fossil fuels. The results of Shuto et al. (2015) suggest that the energy requirements for BMED with HCl and NaOH products will be ~1,390 kWh/tonne PCC, meaning that fugitive emissions will be less than that of the conventional production method (623
kWh/tonne PCC and 210 kg CO₂/tonne PCC)\textsuperscript{35} if the source of electrical energy emits less than 0.15 kg CO₂/kWh (i.e. ~25% less than natural gas).

Future work could include the investigation of a more universal cement recovery method, this could involve adjusting the crushing size, using other types of comminution equipment, or utilizing other thermal or chemical cement removal methods that were described in Chapter 2. Ultimately, the best materials to use are those recovered from waste concrete aggregate recycling facilities. The cement within the coarser fractions of the crushed waste concrete can also be targeted for recovery and carbonation. Future work should also seek to improve the energy efficiency of BMED, given that it is the main energy consuming step and Shuto et al. (2015) suggested that the theoretical minimum energy consumption is associated with dissociation of water, which translates to 444 kWh/tonne PCC.

5.2 Calcium Leaching

Hydrochloric acid was used to leach calcium from waste cement in these experiments because previous authors did not exceed a leaching efficiency of 60% with weaker solvents such as nitric acid (Shuto et al., 2014), acetic acid (Yamasaki et al., 2006 and Shuto et al., 2015), or ammonium salts (Kodama et al., 2008). Calcium was completely leached from Dp<425 µm particles by HCl when the molar ratio of HCl added to calcium and magnesium in the solids was 2:1 (i.e. the stoichiometric amount to dissolve all the calcium and magnesium). Other metals such as aluminum, iron, manganese and magnesium were also leached by HCl; the levels of these dissolved impurities increased with increasing calcium leaching efficiency and acidity. Silicon was also leached but was not quantified by the analytical method.

Although high purity CaCl₂ solutions were produced when ~25% of the calcium was leached and the solution was alkaline, there is merit to leaching and carbonating 100% of the

\textsuperscript{35} From Teir et al. (2005) and Eloneva et al. (2012)
calcium. This is because without chemical processing, the waste concrete passive carbonation models by Pade and Guimaraes (2007) predicted that 37-86% of the cement calcium will be carbonated 30 years after demolition (with a 70 year service life). Therefore leaching and carbonating 100% of the calcium may have a stronger influence on climate change mitigation than lower efficiencies by carbonating waste cement that would not otherwise passively carbonate within 30 years.

This also emphasizes that mitigating fugitive emissions by switching to an electrochemical PCC production process with low carbon energy is the most effective and verifiable emission reduction strategy. Furthermore, since Pade and Guimaraes (2007) also described that the depth of passive carbonation is proportional to the square root of exposure time, there is also likely more merit to recovering the cement from coarser particles for chemical processing because passive carbonation would be inhibited by particle size. This is an additional reason to target the cement in coarser fractions of crushed waste concrete for calcium leaching and carbonation in future work.

Alternative mixing methods during leaching should also be investigated in future work in order to avoid the energy penalty associated with using a continuously stirred reactor. Future work should also seek to verify that HCl does in fact leach calcium significantly more efficiently that other solvents such as acetic acid by using consistent methods and the same batch of waste cement, rather than relying on literature review for solvent comparison.

5.3 Purification

In order to obtain a high calcium extraction efficiency and simultaneously produce PCC with a high degree of whiteness (i.e. marketable qualities), a purification step was used to remove discolouring impurities (namely iron and manganese) before the CaCO₃ precipitation step. Impurities of aluminum, iron, manganese and magnesium were preferentially precipitated by adding alkalinity. The impurities may have precipitated as amorphous silicates due to the co-
leaching of silica (from calcium silicate hydrate) and its subsequent dissociation as the pH increased. It is unclear if the typically slow kinetics of silicate precipitation played an important role in purification step, however other studies on water purification describe silicate precipitation as a possibility as alkalinity is added (Sheikholeslami and Bright, 2002).

Adjusting the pH to 9 removed iron and manganese to such a level that a bright CaCO$_3$ was produced, however a slightly higher pH is required to remove manganese to levels below the detection limits of ICP-OES (0.05 ppm). The most prevalent impurity was magnesium, which can be significantly removed from solution by increasing the pH to 11.0.

However, the removal of magnesium is considered potentially unnecessary and counters sustainability objectives. This is because MgCO$_3$ has similar physical properties as CaCO$_3$, and since the source magnesium mineral was already carbonated, the precipitation of magnesium silicate in the purification step releases CO$_2$ through mineral decarbonation. Furthermore, the molar ratio of Ca$^{2+}$ to Mg$^{2+}$ in solution was as approximately 9:1 when all the calcium was dissolved, therefore at least 10% of the energy consumed to generate HCl would not be utilized if magnesium was removed.

Adding Ca(OH)$_2$ as a purification agent to reach pH 11.0 might remove magnesium while allowing the recovery of some of the purification agent in the final product, however was calcium incorporated into the purification residue even when NaOH was added as a purification agent and the solubility of Ca(OH)$_2$ was not exceeded. This is may be due to the precipitation of amorphous calcium silicate. This suggests that if low magnesium PCC is required for market acceptance then more attention should be paid to silicon leaching and the precipitation of calcium silicate in the purification step, particularly if there is an abundance of silicon due to the production of a silicic colloid in the leaching step. Of note for future work is that previous authors found that less silicon was leached at higher temperatures, which was explained by enhanced adsorption (Bao et al. 2010).
The incorporation of trace elements into the PCC does not appear to be a significant hazard, provided that the leaching solutions are purified to approximately pH 9.0, or ideally slightly higher to minimize manganese content. Barium levels in the PCC may have been slightly higher than the limit for pharmaceutical grade PCC, however this is likely not a significant hazard for use in paper manufacturing and the barium may have been incorporated as less soluble (i.e. less hazardous) compounds than BaCO$_3$. Future work can further study the solubility the trace elements by measuring redox potential and using PHREEQC (a program for chemical speciation and solubility calculations). The solubility of trace elements and chloride from the residual products in water can also be measured.

5.4 Precipitation

The precipitation of CaCO$_3$ and MgCO$_3$ was induced by the addition of Na$_2$CO$_3$(aq), which can be produced through the absorption of CO$_2$(g) by NaOH(aq). Rhombohedral calcite and spherical vaterite CaCO$_3$ particles were precipitated when the solutions contained low levels of magnesium, and the vaterite transformed into rhombohedral calcite with additional reaction time. The size of the rhombodedral calcite particles was larger than what is typically used in paper manufacturing, however the size of the particles was significantly reduced when magnesian calcite, possibly with some amorphous content, was produced from solutions that were purified to pH 9.0. These smaller, high magnesium particles appeared to remain stable for at least 24 hours in water. Future work could include further measurement and optimization of the physical properties of the PCC, namely particle size, surface area, brightness and abrasiveness.
References


Appendix A: Literature Review of Mineral Carbonation Methods

Hydrochloric Acid Route with Serpentine:

Some of the earliest work in aqueous mineral carbonation was done by Lackner et al. (1995) where the authors proposed the use of hydrochloric acid to extract magnesium or calcium from naturally occurring silicate minerals before carbonation. The concept was that this method could be used to capture the CO$_2$ being produced by a thermal power plant and store it in a stable and solid form. In this process, magnesium minerals (such as serpentine) are dissolved by hydrochloric acid, producing a magnesium chloride solution and a silica gel:

$$6\text{HCl}_{(aq)} + \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4(s) \rightarrow 3\text{MgCl}_2(aq) + 2\text{SiO}_2(s) + 5\text{H}_2\text{O}(l)$$

Lackner and colleagues explained that the solution could be boiled to remove water and excess acid, and that heating the solution to 150°C would result in the decomposition of magnesium chloride, regenerating hydrochloric acid:

$$\text{MgCl}_2\cdot6\text{H}_2\text{O}(s) \rightarrow \text{Mg(OH)}\text{Cl}(s) + \text{HCl}(g) + 5\text{H}_2\text{O}(g)$$

The Mg(OH)Cl solids are then dissolved in water which results in the formation of a magnesium chloride solution and magnesium hydroxide solids:

$$2\text{Mg(OH)Cl}_2(s) \rightarrow \text{Mg(OH)}_2(s) + \text{MgCl}_2(aq)$$

The magnesium chloride solution can then be cycled back to the second step, and the magnesium hydroxide precipitate is ready for carbonation:

$$\text{Mg(OH)}_2(s) + \text{CO}_2(g) \rightarrow \text{MgCO}_3(s) + \text{H}_2\text{O}(g)$$

This process was assessed by the National Energy Technology Laboratory (NETL) and International Energy Agency (IEA) and it was concluded that it would take four times the energy produced by burning a unit of coal to capture the CO$_2$ produced by combusting the coal. This negative CO$_2$ balance was said to be the product of the high energy demand for the second boiling/thermal decomposition step (reviewed in Gerdemann et al., 2007). Although the heat
requirement is high, Lackner (2002) stated that through process integration an energy penalty of
under 40% would be placed on a power plant using this CO$_2$ sequestration method since only low
grade heat is required.

Park et al. (2003) investigated the dissolution of serpentine in various solvents and the
carbonation of the dissolved magnesium under high pressure CO$_2$. The authors found that an
extraction solution that contained a mixture of 1 vol% orthophosphoric acid, 0.9 wt% of oxalic
acid and 0.1 wt% EDTA dissolved more magnesium than HCl or acetic acid; and that HCl
extracted slightly more than acetic acid. High temperatures (~70°C) were also found to enhance
magnesium extraction. The conversion of Mg$^{2+}$ to MgCO$_3$ was limited under high pressure CO$_2$
when the aqueous phase was fairly acidic because carbonic acid was not dissociated.

Since the dissolution of calcium and magnesium silicates is favoured in acidic conditions,
and precipitation is favoured in alkaline conditions, Park and Fan (2004) proposed and tested a
“pH swing” process where the pH was increased through the addition of NH$_4$OH after the
dissolution step and before the carbonate precipitation step. The pH was first increased dropwise
to ~8.6 to precipitate iron oxide from solution, which was then separated. This was done because
the authors wished to recover a relatively high purity MgCO$_3$ that could be sold to reduce the
costs of the carbon sequestration scheme. After iron was removed, pure CO$_2$ was bubbled
through the system at 1 atm, and the pH was further increased to ~9.5 with additional NH$_4$OH to
promote precipitation.

Park and colleagues also identified the formation of a passivating SiO$_2$ layer to be an
extraction limiting phenomena. To overcome the SiO$_2$ barrier, Park and Fran (2004) conducted
their extraction experiments with the aid of an internal grinding system that consisted of 20%
volume 2mm glass beads in a fluidized bed reactor. This internal grinding system was found to
dramatically improve the extent of magnesium extraction under acidic conditions. After 1h of the
dissolution process, 65% of the magnesium was extracted. Other methods of internal grinding
have been found be effective at exfoliating the SiO$_2$ layer, such as increasing the solid to liquid ratio to >5% solids under aggressive stirring conditions (Bearat et al., 2006).

**Acetic Acid Route with Wollastonite:**

Kakizawa et al. (2001) reviewed the HCl process described by Lackner et al. (1995), and proposed that the energy penalty of the HCl method might be avoided by using an acid that will spontaneously regenerate when exposed to high pressure CO$_2$. Acetic acid (pKa = 4.76) was selected because it is stronger than silicic acid (pKa = 9.5), and can therefore extract calcium and magnesium ions from the silicates. Acetic acid is also weaker than carbonic acid (pKa = 3.6), and therefore can be replaced by carbonic acid during the crystallization process. Pulverized wollastonite rock was chosen as the calcium source. The acetic acid is regenerated by adding high pressure CO$_2$, and the calcium is precipitated as CaCO$_3$. The process was explained with the following reactions:

\[
\text{CaSiO}_3 + 2\text{CH}_3\text{COOH} \rightarrow \text{Ca}^{2+} + 2\text{CH}_3\text{COO}^- + \text{H}_2\text{O} + \text{SiO}_2
\]

\[
\text{Ca}^{2+} + 2\text{CH}_3\text{COO}^- + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + 2\text{CH}_3\text{COOH}
\]

Kakizawa et al. (2001) conducted experiments on calcium extraction and found that 48% of the calcium in the wollastonite particles could be extracted in 250 minutes. The influence of particle size on reaction rate was also investigated, and a linear relationship was found between extraction efficiency after 30 minutes and the reciprocal of the particle diameter. The extraction rate decreased after about 60 minutes which was said to be due to the formation of a passivating SiO$_2$ layer on the particles, thus they concluded that intensive pulverization was required to achieve high calcium extraction efficiencies.

The authors calculated that the precipitation step should proceed spontaneously at a CO$_2$ partial pressure of 1 bar and a temperature of 298K (25ºC). Kakizawa and colleagues also stated that the conversion ratio of dissolved calcium to CaCO$_3$ should be dependent on CO$_2$ pressure. They predicted that at atmospheric pressure a conversion ratio of 40% could be achieved, while a
CO₂ pressure of 30 bar could reach 75% conversion. The experimental results however, showed that only about 20% of the dissolved calcium could be converted to CaCO₃ at CO₂ pressure of 30 bar. The rate of crystallization decreased with time, which was explained by the re-dissolution of the precipitated CaCO₃ particles as the solution became more acidic. The authors estimated that with this process the CO₂ produced by a 100 MW thermal power plant could be captured at an operational parasitic energy cost of 20.4MW. Approximately 75% of the energy used in the process was split evenly between CO₂ separation with MEA scrubbing, CO₂ compression to 30 bar, and the pulverization of wollastonite from 1000µm to 20µm. The remaining ~25% was accounted by the operation of a stirred-tank reactor and recovering CaCO₃ by pressurized filtration. The transportation of feed materials and product was not included in the energy analysis.

Teir et al. (2005) modelled various mineral carbonation processes that had been proposed and the authors concluded that the acetic acid route described by Kakizawa (2001) was the most promising method for sequestering CO₂ through mineral carbonation. They were interested in reducing the CO₂ emissions from the pulp and paper industry by producing precipitated calcium carbonate (PCC) through the carbonation of wollastonite. Typically the production of PCC uses mined and crushed high purity limestone as raw material, which is then calcined and re-carbonated.

**Acetic Acid Route with Alkaline Industrial Wastes:**

In addition to conserving resources and managing waste, the use of industrial waste streams such as steelmaking slags or waste cement in mineral carbonation processes offers several potential benefits. These include their low cost and that in the case of waste cement, finely ground particles can be obtained from existing practices without additional pulverization (Shuto et al., 2014). An additional advantage of using alkaline industrial waste instead of natural
minerals is that industrial wastes are typically more chemically reactive than naturally occurring minerals (Teir et al. (2007), Yamasaki et al. (2006) and Abe et al. (2013)).

To overcome the low reactivity and limited availability of wollastonite, Teir et al. (2007) investigated the dissolution of calcium from steelmaking slags in acetic acid. The authors found that the dissolution of impurities from various slags was an issue, and suggested that this needed to be solved in order to produce a high purity and marketable calcium carbonate. The molar ratio of acetic acid to calcium can be calculated to be an excess of ~40 moles of acetic acid per mole of calcium. The authors also found that a silica gel formed in strong acetic acid solutions (33% acetic acid) at temperatures above 70°C, and that it could be removed by mechanical filtration.

The research group then proceeded to study the effect of the acetic acid concentration (i.e. the acid to calcium molar ratio) and temperature on the dissolution of calcium and impurities from steel converter slag. It should be noted that the authors chose steel converter slag over the more soluble blast furnace slag because blast furnace slag is already accepted as a raw material in cement manufacturing. They also investigated the precipitation of calcium carbonate by bubbling CO₂ through the solution (Eloneva et al., 2008). In this study it was found that weak solutions of acetic acid could dissolve approximately 30% of the calcium fairly selectively, while a maximum calcium extraction efficiency of approximately 90% could be reached with stronger solutions (i.e. a higher acid:calcium ratio). The stronger solutions also dissolved significant amounts of undesirable impurities. Solution temperature (30°C-70°C) was not found to have a significant influence on the dissolution of steel slag in acetic acid, however Bao et al. (2010) found that Fe, Al and Si impurities were significantly removed from solution after 1h at higher temperatures (80°-94°C). Bao et al. (2010) also found that the extraction efficiency of calcium and magnesium by acetic acid was enhanced as temperatures increased from 40-94°C.

In order to effectively precipitate calcium carbonate Eloneva et al. (2008) found the addition of sodium hydroxide to be necessary because acetic acid was regenerated by CO₂ while
calcium carbonate was precipitated, thus a lowering pH prevented further precipitation of calcium carbonate (just as in Kakizawa et al. (2001)). It was explained that when sodium hydroxide was added, calcium acetate was converted to calcium hydroxide and sodium acetate. The sale of sodium acetate was considered instead of recycling it.

Through the addition of sodium hydroxide to calcium acetate (i.e. the formation and subsequent carbonation of Ca(OH)$_2$ particles), Eloneva et al. (2008) were able convert 31-86% of the calcium into calcium carbonate with a purity of over 99%. The calcium carbonate particles precipitated at 30°C were found to have rhombohedral shapes, very high brightness, and a mean particle size of 0.6 µm. It should be noted that based on the results of Gao et al. (2007), the formation of fine particles (<<5µm) was more likely related to the precipitation mechanism (carbonation of Ca(OH)$_2$ by CO$_2$ in alkaline conditions) rather than due to having a precipitation temperature of 30°C. It was suggested that flue gases could be used as a CO$_2$ source without the need for an energy-intensive CO$_2$ separation because the precipitation yield was not significantly affected by temperature (30°C-70°C), CO$_2$ pressure (1-30 bar), gas flow rate, or CO$_2$ concentration.

Eloneva et al. (2008) also conducted a feasibility analysis where it was calculated that producing 1 tonne of pure calcium carbonate (storing 0.44 tonnes of CO$_2$) with this method would consume 4.8 tonnes of steel slag, 1.4 tonnes of acetic acid, and 0.9 tonnes of sodium hydroxide and produce 1.9 tonnes of sodium acetate. The chemical costs were then calculated to be as much as $1,350 US$\textsuperscript{36} per tonne of calcium carbonate, assuming the sodium acetate by-product could be resold for $460 US$\textsuperscript{37} per tonne. Typical values for PCC sales are below $500 US per tonne. Although the calcium carbonate product had a particle size (0.6 µm) that was almost sufficient to qualify as an nano grade PCC (<0.1 µm), Eloneva (2010) stated that the costs related to the

\textsuperscript{36} Calculated from €1,990 with a 2008 exchange rate of 1.471366 EUR/USD
\textsuperscript{37} Calculated from €680 with the same exchange rate as above
consumption of chemicals was in excess of the value of nano PCC. It was concluded that this acetic acid + sodium hydroxide process was not economically feasible mainly because the use of sodium hydroxide to enable the precipitation of calcium carbonate prevents efficient recycling of the chemicals.

**High Pressure CO\(_2\) Process with Waste Cement:**

A mineral sequestration method has been developed in Japan that utilizes waste cement and pressurized CO\(_2\) sourced from a thermal power plant (Katsuyama et al., 2005). The method utilizes a pressure swing process in order to first dissolve the calcium in cement (i.e. mostly from alite, belite and portlandite) and then precipitate high purity calcium carbonate. The high pressure CO\(_2\) in the extraction step creates an acidic solution to dissolve the calcium-rich solid, and then when the CO\(_2\) pressure decreases the acidity of the solution must also decrease, and calcium carbonate is precipitated.

Katsuyama et al. (2005) were able to extract calcium from the waste cement at a rate sufficient to reach close to the saturation value (with respect to CaCO\(_3\)) within 20-30 minutes at CO\(_2\) pressures of 9, 14, and 30 bar. In terms of calcium extraction efficiency, ~75\% of the calcium could be dissolved from waste cement with an excess of water under a CO\(_2\) partial pressure of 30 bar (Iizuka, 2006).

When the CO\(_2\) pressure was lowered for the precipitation step, the calcium was precipitated at a significantly slower rate than it was extracted, but a high purity (~98\%) calcium carbonate was produced. Since the drop in CO\(_2\) pressure created a solution that is supersaturated with respect to CaCO\(_3\), the addition of seed crystals would found to significantly accelerate the precipitation step; the seed crystals also improved the purity of the product from as low as 80\% to ~98\% CaCO\(_3\). The authors estimated the production costs of this method to be as low as $136 US/metric tonne for desulphurization-grade (~98\%) CaCO\(_3\), and $323 US/metric tonne for ultra-high purity (99.9\%) CaCO\(_3\) if the ~98\% pure CaCO\(_3\) was re-processed. The most costly
operations were stated to be the treatment of solid industrial waste, transportation and wastewater treatment. Approximately 90% of the capital costs were associated with the construction of the waste water treatment plant and a silo for the waste cement.

Yamasaki et al. (2006) reviewed this high pressure CO\(_2\) process in terms of power consumption, and stated that 25.9 MW would be required in order to capture the CO\(_2\) produced from a 100 MW thermal power plant (or 421 kWh/t-CO\(_2\)). Yamasaki et al. (2006) also reviewed the acetic acid + waste cement route, and stated the power consumption to be 13.9 MW to capture the CO\(_2\) produced from a 100 MW thermal power plant. The high pressure CO\(_2\) method was explained to consume more power than the acetic acid route due to the pulverization of waste cement and the compression of CO\(_2\). In the acetic acid + waste cement method pulverization was not included in the power calculation because it was assumed that a waste cement powder with an average particle diameter of 100 µm could be recovered from the aggregate recycling process of waste concrete. Pulverization of 5mm diameter particles to 200 µm was considered in the high pressure CO\(_2\) process.

**Table: Breakdown of process energy requirements, adapted from Yamasaki et al. (2006).**

<table>
<thead>
<tr>
<th></th>
<th>Wollastonite + acetic acid</th>
<th>Waste cement + acetic acid</th>
<th>Waste cement + pressurized CO(_2)</th>
<th>kWh/t-CO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CO(_2) separation</strong></td>
<td>5.56</td>
<td>5.56</td>
<td>5.56</td>
<td>89</td>
</tr>
<tr>
<td><strong>CO(_2) compression</strong></td>
<td>4.65</td>
<td>4.65</td>
<td>13.7</td>
<td>223</td>
</tr>
<tr>
<td><strong>Pulverization</strong></td>
<td>5.29</td>
<td>-</td>
<td>6.4</td>
<td>104</td>
</tr>
<tr>
<td><strong>Extraction</strong></td>
<td>1.27</td>
<td>0.07</td>
<td>0.32</td>
<td>5</td>
</tr>
<tr>
<td><strong>Crystallization</strong></td>
<td>2.60</td>
<td>2.60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>CaCO(_3) separation</strong></td>
<td>1.01</td>
<td>1.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>20.38</td>
<td>13.89</td>
<td>25.9</td>
<td>421</td>
</tr>
</tbody>
</table>
**Ammonium Salt Process with Steelmaking Slags:**

Kodama et al. (2008) sought to design a new mineral carbonation system with a simple process design, short reaction time, with a lower energy consumption than previous processes. As of 2008, the state of the art in indirect aqueous mineral carbonation was such that researchers were able to promote the dissolution alkaline earth metals from silicates with various extraction agents such as hydrochloric acid (Park et al., 2003) and acetic acid (Eloneva et al., 2008). However, the dissolved metals were unable to efficiently precipitate as carbonate minerals when CO$_2$ was introduced because the acidity of the solutions prevented the dissociation to CO$_3^{2-}$ ions. To overcome the acidity of the solutions, chemical additives were required to increase the pH of the solution, resulting in chemical costs that made the processes economically unfeasible and prevented the recycling of the reaction solution (Eloneva et al., 2008). Other methods utilizing pressurized CO$_2$ to dissolve the alkaline earth metals required over ~310kWh/t-CO$_2$ in order to separate and pressurize the gas to 30 bar (Katsuyama et al., 2005).

Kodama et al. (2008) sought to solve the problem of having an acidic calcium-rich solution by using the pH swing of a weak base-strong acid solution. The process was said to proceed at conditions under 80°C and atmospheric pressure, while enabling the recycling of the reaction solution. The authors used ammonium chloride to extract calcium from steelmaking slag in acidic conditions to produce calcium chloride, a silica residue and ammonia:

$$4\text{NH}_4\text{Cl(aq)} + 2\text{CaO} \cdot \text{SiO}_2(s) \rightarrow 2\text{CaCl}_2(aq) + \text{SiO}_2(s)\downarrow + 4\text{NH}_3(aq) + 2\text{H}_2\text{O(l)}$$

When ammonia is in aqueous solution, it deprotonates a small fraction of water to give ammonium and hydroxide:

$$\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad k_b = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3] = 1.8 \times 10^{-5}$$

The ammonia solution (or ammonium hydroxide) can then act as a CO$_2$ absorbent:

$$4\text{NH}_3(aq) + 2\text{CO}_2(aq) + 2\text{CaCl}_2(aq) + 4\text{H}_2\text{O(l)} \rightarrow 2\text{CaCO}_3(s)\downarrow + 4\text{NH}_4\text{Cl(aq)}$$
Extraction experiments were conducted by Kodama et al. (2008) on steelmaking slag with ammonium chloride; it was found that up to 60% of the calcium could be extracted with high selectivity, and that up to a 98% pure CaCO$_3$ could be produced. It should be noted that the authors calcined the steelmaking slag at 950°C for 30 min before the extraction experiments to remove CO$_2$ and H$_2$O. The authors estimated that this carbon sequestration process would have an energy consumption of 130 kWh/t-CaCO$_3$. The energy consumption breakdown for the process is summarized in the following table:

<table>
<thead>
<tr>
<th>CO$_2$ adsorption</th>
<th>Pulverization</th>
<th>Filtering residue</th>
<th>Filtering CaCO$_3$</th>
<th>Fluid Pump</th>
<th>Steam Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5%</td>
<td>25.3%</td>
<td>19.1%</td>
<td>9.5%</td>
<td>10.6%</td>
<td>32%</td>
</tr>
</tbody>
</table>

This ammonium chloride method was therefore found to be promising compared to previously reported processes, however it was stated to have technical issues involving the evaporative loss NH$_3$ from the CO$_2$ absorber. An additional step to capture the NH$_4$ emissions was suggested that involved adding sulfuric acid to produce ammonium sulfate.

After discovering the limitations of the acetic acid route, a research group from Finland sought an effective calcium-selective solvent that could be fully recovered and reused; the ammonium chloride method was thought to be promising based on the results from Kodama et al. (2008). In addition to ammonium chloride, Eloneva et al. (2009) tested other ammonium salts as calcium-selective solvents. The authors found that ammonium chloride, ammonium acetate and ammonium nitrate could efficiently dissolve calcium from steel converter slag and desulphuization slag (~80% and ~60% respectively); these materials were found to contain some free lime (but mostly calcium silicates) by XRD before leaching. Blast furnace slag and ladle slag were also tested, in these materials all of the calcium was bound in silicates, and the extraction of calcium by the solvents was lower (~10% and ~20% respectively). The XRD

---

38 Calculated from the quoted value of 300 kWh/t-CO$_2$.
results showed that Ca$_2$SiO$_4$ was the dominant phase in steel converter slag and desulphurization slag, while the dominant phases in blast furnace and ladle slag were more complex calcium silicate phases containing aluminum and iron. The authors concluded that the ammonium salt-based method is not suitable for all types of calcium-containing waste products.

**Nitric Acid with Waste Cement:**

A new mineral carbonation process was proposed by Shuto et al. (2014) where a stronger acid could be used to improve the extraction of calcium from silicates, while allowing CaCO$_3$ to be precipitated without the need for energy-intensive high-pressure CO$_2$ or large amounts of sodium hydroxide. In this process calcium is dissolved from waste cement powder by nitric acid, and is precipitated through the introduction of sodium carbonate instead of CO$_2$. The authors proposed that the sodium carbonate could be produced through the adsorption of CO$_2$ by sodium hydroxide. The recycling of nitric acid and sodium hydroxide by bipolar membrane electrodialysis was also demonstrated. The process can be described by the following equations:

$$3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}(s) + 6\text{HNO}_3(aq) \rightarrow 3\text{Ca(NO}_3)_2(aq) + 2\text{SiO}_2(s) + 6\text{H}_2\text{O}$$

$$2\text{NaOH}(aq) + \text{CO}_2(g) \rightarrow \text{Na}_2\text{CO}_3(aq) + \text{H}_2\text{O}$$

$$\text{Ca(NO}_3)_2(aq) + \text{Na}_2\text{CO}_3(aq) \rightarrow \text{CaCO}_3(s) + 2\text{NaNO}_3(aq)$$

$$\text{NaNO}_3(aq) + \text{H}_2\text{O} \rightarrow \{\text{NaOH}(aq)\} + \{\text{HNO}_3(aq)\}$$

The authors used real waste cement powder that was sampled from a waste concrete aggregate recycling plant in Japan. The sample was sieved and particles less than 212 µm where used in the extraction experiments; the material was said to contain mostly hydrated cement powder. The waste cement powder was found to contain calcium (32.3%), silicon (11.5%), aluminum (2.0%), iron (1.8%), magnesium (0.5%), sodium (0.4%), potassium (0.3%) and sulphur (0.3%) by mass.

In the calcium-extraction experiments the authors found that the molar ratio of nitric acid to calcium (N/Ca) was the most important variable in the leaching experiments. The authors
experimented with N/C ratios ranging from 0.38 to 7.7. Calcium was rapidly leached in the first 10 minutes in all cases where N/Ca ranged from 0.38 to 7.7, and was essentially constant after that for 24 hours. The maximum yield of calcium was found to be approximately 45%, even when with a large excess of nitric acid. The authors found that impurities of silicon, iron and aluminum were initially leached but were removed from solution over ~120 minutes when the N/C ratio was \( \leq 0.77 \). However when the N/C was \( \geq 1.5 \), the solution was acidic and approximately 30% of the silicon, and 40% of the iron and aluminum were leached and remained in solution over time. A higher final pH corresponded to a higher mass fraction of calcium in solution (less impurities), the highest reported solution pH was ~9.0 when the N/C was 0.38. More acidic solutions were produced as the calcium extraction efficiency increased with increasing N/C.

In experiments with a fixed N/Ca ratio of 0.65, various initial concentrations (0.3M-3.0M) of nitric acid were tested. Calcium was extracted at the same rate with all the solutions, and after 10 minutes approximately 30% was extracted in all cases; calcium levels essentially flat-lined after 10 minutes. The authors found the pH of the solution would increase more rapidly with higher initial concentrations of nitric acid, obtaining a high mass fraction of calcium in solution more quickly. However after two hours of mixing, all solutions had essentially the same pH (near neutral) and mass fraction of calcium. Specifically, a solution with an initial nitric acid concentration of 0.6 M was found to reach a high (~99.5%) calcium purity in ~10 minutes, while a solution with an initial nitric acid concentration of 0.3 M was found to reach about the same purity in 2 hours. The rate of pH change did not correlate with the rate of calcium extraction, as the calcium was quickly leached in the first 10 minutes and the pH continued to increase while the calcium concentration in solution remained constant.

Although not explained by the authors, the increase in pH and mass fraction of calcium in solution overtime could be explained by the removal of aluminum and iron from solution over
time. This explanation is justified because under similar conditions the authors also showed that aluminum, iron, and silicon were removed from solution over time, and iron and aluminum can form complexes with water and act as weak acids. Therefore increasing the acid concentration with a fixed N/Ca ratio might increase the rate at which impurities are removed by improving mechanical mixing, since a lower solution volume is used at higher acid concentrations.

The authors also pointed out that before Na₂CO₃ is added to precipitate CaCO₃, it is important for the pH of the solution to be greater than 6.35 because under acidic conditions gaseous CO₂ will be released. This is because a pH of 6.35 corresponds the pKₐ₁ value of carbonic acid.

Shuto et al. (2014) also conducted a CaCO₃ precipitation experiment. The authors started by leaching the calcium from waste cement using a N/Ca ratio of 0.65 (an excess of calcium), and an initial nitric acid concentration of 3.0M. The final pH of the leaching solution was 7.2 and ~30% of the calcium was extracted. This solution was then mixed with 1.5M sodium carbonate to precipitate calcium carbonate. Approximately 99.3% of the calcium was precipitated, and the final calcium concentration was 378 mg/L. The purity of the CaCO₃ was found to be >94%, as measured by the weight loss between 600°C - 800°C from TGA, and the diameter of the particles was about 10 µm.

Solely based on the results of the electrodialysis experiments, the authors calculated that 3800 kWh would be required to capture 1 tonne of CO₂ (or 1672 kWh/tonne CaCO₃). This is equivalent to 300kJ/mol NaOH, and since theoretical power consumption was only 80.1kJ/mol NaOH the authors stated that future work will seek to improve the efficiency of electrodialysis. The electrodialysis results demonstrated that lower concentrations of the feed salt would be favourable because a higher recovery ratio of acid and base can be achieved with lower power consumption.
Comparison of solvent extraction efficiencies

Comparing the extraction efficiency of different solvents by referencing studies from various authors is difficult primarily due to differences in mineralogy and also the acid to Ca (and/or Mg) ratio, and grain size. Therefore the best comparison of solvent extraction efficiency was found in the doctoral dissertation by Teir (2008) where a consistent material was used for several solvents at multiple concentrations. The author found that H$_2$SO$_4$ and HCl extracted ~25% of the magnesium from serpentine (74 µm<Dp<125 µm) after one hour of leaching at 20°C, while HNO$_3$ extracted ~17.5%, CH$_3$COOH extracted ~4% and ammonium salts extracted <1%. The author also found that increasing temperature significantly enhanced magnesium leaching with HCl, and that leaching efficiency was negatively affected when particle sizes exceeded 0.125 mm.

Solvay Process Modification (“Dual Alkali Approach”)

Huang et al. (2001) proposed the production and storage of Na$_2$CO$_3$ for CCS through a “dual alkali” approach that is based on the Solvay process (i.e. the industrial production of Na$_2$CO$_3$). In the Solvay process sodium bicarbonate is produced by using ammonia to catalyze the reaction between CO$_2$ and sodium chloride; the process can be described by the following reactions:

$$\text{CO}_2 + \text{NaCl} + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3\downarrow + \text{NH}_4\text{Cl}$$

The CO$_2$ is conventionally sourced from calcining limestone, and following the reaction precipitated sodium bicarbonate is separated by filtration. Sodium carbonate is then obtained by heating sodium bicarbonate and releasing half of the absorbed CO$_2$. Ammonia is recovered by reacting ammonium chloride with the lime that was produced in the calcination step:

$$2\text{NH}_4\text{Cl} + \text{Ca(OH)}_2 \rightarrow 2\text{NH}_3 + \text{CaCl}_2 + 2\text{H}_2\text{O}$$

Huang et al. (2001) explained that the main drawback of using CO$_2$ from thermal power plants as substitute for the CO$_2$ conventionally sourced from calcination is that lime is still
required to regenerate ammonia. This was stated to be a problem because in addition to being energy intensive, one mole of CO$_2$ from the calcination of limestone is released for every two moles of CO$_2$ that is captured from power plant emissions.

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]

\[
2\text{NaCl} + 2\text{CO}_2 + \text{CaO} + \text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3 + \text{CaCl}_2
\]

Huang et al. (2001) sought to circumvent the drawbacks of the Solvay process, to do so they investigated the replacement of ammonia with an amine solution, and also a separate method of replacing lime with activated carbon to regenerate ammonia. The authors found that methylaminoethanol (MAE) was an effective alkali for CO$_2$ absorption from a 10% CO$_2$ feed gas in the presence of sodium chloride, and resulted in the precipitation of sodium bicarbonate; however the authors did not identify a suitable alkali to regenerate MAE. Activated carbon was found to regenerate ammonia at ambient temperatures by decomposing NH$_4$Cl into HCl and NH$_3$ and increased the solution pH from 4.7 to 9.5. The basicity of the activated carbon was said to be responsible for the adsorption of HCl molecules from the NH$_4$Cl solution:

\[
\text{NH}_4\text{Cl} + \text{AC} \leftrightarrow \text{NH}_3 + \text{AC} \cdot \text{HCl}
\]

The recycling of the activated carbon and removal of the adsorbed HCl was also demonstrated by water extraction:

\[
\text{AC} \cdot \text{HCl} + \text{H}_2\text{O} \leftrightarrow \text{AC} + \text{HCl} \cdot \text{H}_2\text{O}
\]

The enthalpy of the adsorption of hydrochloric acid by activated carbon was stated by Huang et al. (2001) to be -5.94 kcal/mol, and therefore the enthalpy of desorption is +5.94 kcal/mol which is significantly less than that for the desorption of CO$_2$ from an MEA-carbamate (+17.22 kcal/mol). Huang et al. (2001) found the desorption rate of HCl from activated carbon increased with increasing temperature, and that 41.8% of the HCl desorbed at 100°C and 8.36% at 20 °C. Therefore the process described by Huang et al. (2001) can produce both Na$_2$CO$_3$ and HCl. Although the authors proposed the storage of CO$_2$ as Na$_2$CO$_3$, it could be stored as CaCO$_3$ instead.
if the HCl was used to dissolve calcium silicates, and the resulting CaCl$_2$ solution was mixed with the Na$_2$CO$_3$. The process described by Kodama et al. (2008) is also essentially a modified Solvay process.
### Table A-1: ICP-OES results from the leaching solutions with HCC fine particles and various volumes of 0.5 M HCl.

<table>
<thead>
<tr>
<th>Material Type</th>
<th>HCl:(Ca+Mg)</th>
<th>HCC Fines</th>
<th>HCC Fines</th>
<th>HCC Fines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4</td>
<td>0.8</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Sample (ug/g)</td>
<td>leach</td>
<td>pur.</td>
<td>ppt.</td>
<td>leach</td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>3.60</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>B</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Ba</td>
<td>1.10</td>
<td>&lt;0.05</td>
<td>1.10</td>
<td>1.00</td>
</tr>
<tr>
<td>Be</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>9740</td>
<td>3.00</td>
<td>9610</td>
<td>9350</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>0.200</td>
<td>0.0980</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0650</td>
<td>0.120</td>
<td>0.0610</td>
<td>0.05</td>
</tr>
<tr>
<td>K</td>
<td>101</td>
<td>61.4</td>
<td>77.2</td>
<td>79.8</td>
</tr>
<tr>
<td>Mg</td>
<td>31.9</td>
<td>0.520</td>
<td>377</td>
<td>359</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>1.70</td>
<td>1.00</td>
</tr>
<tr>
<td>Mo</td>
<td>0.0750</td>
<td>&lt;0.05</td>
<td>0.0660</td>
<td>0.0690</td>
</tr>
<tr>
<td>Na</td>
<td>127</td>
<td>6500</td>
<td>81.2</td>
<td>80.3</td>
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<tr>
<td>Ni</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>P</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>S</td>
<td>238</td>
<td>114</td>
<td>216</td>
<td>206</td>
</tr>
<tr>
<td>Sb</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Se</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Sn</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Sr</td>
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<td>0.0280</td>
<td>13.7</td>
<td>13.3</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Tl</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
</tr>
<tr>
<td>U</td>
<td>0.270</td>
<td>0.330</td>
<td>0.270</td>
<td>0.250</td>
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<tr>
<td>V</td>
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<td>0.120</td>
</tr>
<tr>
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<td>0.0570</td>
<td>0.0140</td>
<td>0.0390</td>
</tr>
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<td>pH</td>
<td>10.42</td>
<td>10.82</td>
<td>7.45</td>
<td>8.93</td>
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<tr>
<td>Volume (mL)</td>
<td>75</td>
<td>150</td>
<td>150</td>
<td>150</td>
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</table>
Table A-2: ICP-OES results from the leaching solutions with HCC coarse particles and various volumes of 0.5 M HCl.

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<th>HCC Coarse</th>
<th>HCC Coarse</th>
<th>HCC Coarse</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>HCl/(Ca+Mg)</td>
<td>leach pur.</td>
<td>leach pur.</td>
<td>leach pur.</td>
</tr>
<tr>
<td>Sample (ug/g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>2.20</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>B</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Ba</td>
<td>1.10</td>
<td>&lt;0.05</td>
<td>1.40</td>
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<td>Be</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
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<td>Ca</td>
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<td>&lt;0.025</td>
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<td>Cr</td>
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<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
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<td>0.860</td>
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<tr>
<td>Mg</td>
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<td>&lt;0.05</td>
<td>5.00</td>
</tr>
<tr>
<td>Mo</td>
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<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
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<td>&lt;0.3</td>
<td>&lt;0.3</td>
</tr>
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<td>P</td>
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<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
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<td>Pb</td>
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<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
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<td>102</td>
<td>222</td>
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<td>&lt;0.1</td>
<td>&lt;0.1</td>
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<tr>
<td>Se</td>
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<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Sn</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Sr</td>
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<td>0.0320</td>
<td>14.1</td>
</tr>
<tr>
<td>Ti</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Tl</td>
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<td>&lt;0.025</td>
<td>&lt;0.025</td>
</tr>
<tr>
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<td>0.300</td>
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<td>Zn</td>
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<td>0.0110</td>
<td>0.0400</td>
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<tr>
<td>pH</td>
<td>10.56</td>
<td>10.81</td>
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</tr>
<tr>
<td>Volume (mL)</td>
<td>75</td>
<td>150</td>
<td>150</td>
</tr>
</tbody>
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Table A-3: ICP-OES results on leaching solutions with LCC fines and various volumes of 0.5 M HCl.

<table>
<thead>
<tr>
<th>Material Type</th>
<th>LCC Fines</th>
<th>LCC Fines</th>
<th>LCC Fines</th>
<th>LCC Fines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCl:(Ca+Mg)</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Sample (ug/g)</td>
<td>leach</td>
<td>pur.</td>
<td>ppt.</td>
<td>leach</td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>27.2</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>B</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>1.40</td>
</tr>
<tr>
<td>Ba</td>
<td>2.10</td>
<td>&lt;0.05</td>
<td>1.60</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Be</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>10000</td>
<td>3.50</td>
<td>10300</td>
<td>3.10</td>
</tr>
<tr>
<td>Cd</td>
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<td>&lt;0.025</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.100</td>
</tr>
<tr>
<td>Cr</td>
<td>0.360</td>
<td>0.150</td>
<td>0.0900</td>
<td>0.0400</td>
</tr>
<tr>
<td>Cu</td>
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<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0820</td>
<td>0.140</td>
<td>0.0510</td>
<td>0.0520</td>
</tr>
<tr>
<td>K</td>
<td>480</td>
<td>199</td>
<td>223</td>
<td>110</td>
</tr>
<tr>
<td>Mg</td>
<td>2.40</td>
<td>0.450</td>
<td>235</td>
<td>9.40</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>32.5</td>
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<td>Mo</td>
<td>0.0920</td>
<td>&lt;0.05</td>
<td>0.0740</td>
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<tr>
<td>Na</td>
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<td>6330</td>
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<td>&lt;0.3</td>
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<td>&lt;1.0</td>
<td>&lt;1.0</td>
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<td>Pb</td>
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<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>0.0320</td>
</tr>
<tr>
<td>S</td>
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<td>293</td>
<td>182</td>
</tr>
<tr>
<td>Sb</td>
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<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Se</td>
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<td>&lt;0.1</td>
<td>&lt;0.1</td>
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</tr>
<tr>
<td>Sn</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Sr</td>
<td>23.5</td>
<td>0.0430</td>
<td>20.6</td>
<td>0.0020</td>
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<tr>
<td>Ti</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
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<td>0.0180</td>
</tr>
<tr>
<td>Tl</td>
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<td>&lt;0.025</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
</tr>
<tr>
<td>U</td>
<td>0.260</td>
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<td>0.260</td>
<td>&lt;0.2</td>
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<tr>
<td>V</td>
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<td>&lt;0.02</td>
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<td>0.0620</td>
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<tr>
<td>Zn</td>
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<td>0.0140</td>
<td>0.0170</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>pH</td>
<td>11.00</td>
<td>10.80</td>
<td>9.34</td>
<td>10.83</td>
</tr>
<tr>
<td>Volume (mL)</td>
<td>75</td>
<td>150</td>
<td>150</td>
<td>300</td>
</tr>
</tbody>
</table>
Table A-4: ICP-OES results of leaching solutions with LCC coarse and various volumes of 0.5 M HCl.

<table>
<thead>
<tr>
<th>Material Type</th>
<th>LCC Coarse 0.6</th>
<th>LCC Coarse 0.6</th>
<th>LCC Coarse 1.2</th>
<th>LCC Coarse 2.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl(Ca+Mg)</td>
<td>leach pur. ppt.</td>
<td>leach pur. ppt.</td>
<td>leach pur. ppt.</td>
<td>leach pur. ppt.</td>
</tr>
<tr>
<td>Ag</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Al</td>
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<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>As</td>
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<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>B</td>
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<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Ba</td>
<td>1.60</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Be</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Ca</td>
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<td>10000</td>
<td>9770</td>
</tr>
<tr>
<td>Cd</td>
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<td>&lt;0.025</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
</tr>
<tr>
<td>Co</td>
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<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Cr</td>
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<td>0.140</td>
<td>0.300</td>
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</tr>
<tr>
<td>Cu</td>
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<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0540</td>
<td>0.110</td>
<td>0.0680</td>
<td>0.100</td>
</tr>
<tr>
<td>K</td>
<td>269</td>
<td>136</td>
<td>278</td>
<td>126</td>
</tr>
<tr>
<td>Mg</td>
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<td>0.430</td>
</tr>
<tr>
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<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
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<td>0.0670</td>
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<tr>
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<td>6780</td>
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<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>P</td>
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<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Pb</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>S</td>
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<td>160</td>
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<td>154</td>
</tr>
<tr>
<td>Sb</td>
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<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Se</td>
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<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Sn</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Sr</td>
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<td>0.0190</td>
<td>21.6</td>
<td>0.0420</td>
</tr>
<tr>
<td>Ti</td>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Tl</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
<td>&lt;0.025</td>
</tr>
<tr>
<td>U</td>
<td>0.240</td>
<td>&lt;0.2</td>
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<td>&lt;0.2</td>
</tr>
<tr>
<td>V</td>
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<td>&lt;0.02</td>
<td>0.130</td>
<td>&lt;0.02</td>
</tr>
<tr>
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<td>0.0360</td>
<td>0.0230</td>
<td>0.0180</td>
</tr>
<tr>
<td>pH</td>
<td>10.73</td>
<td>10.85</td>
<td>10.67</td>
<td>10.55</td>
</tr>
<tr>
<td>Volume (mL)</td>
<td>75</td>
<td>150</td>
<td>75</td>
<td>150</td>
</tr>
</tbody>
</table>

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Appendix C: ICP-OES Results (Solids)

Table A-5: ICP-OES results on the chemical analysis of waste concrete materials after digestion in aqua regia.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Low Carbonate Concrete (LCC)</th>
<th>High Carbonate Concrete (HCC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>µg/g</td>
<td>Fine (Dp&lt;105µm)</td>
<td>Coarse (105µm&lt;Dp&lt;425µm)</td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>Al</td>
<td>19000</td>
<td>14000</td>
</tr>
<tr>
<td>As</td>
<td>2.4</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>B</td>
<td>39.4</td>
<td>25</td>
</tr>
<tr>
<td>Ba</td>
<td>320</td>
<td>220</td>
</tr>
<tr>
<td>Be</td>
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<td>&lt;4.0</td>
</tr>
<tr>
<td>Ca</td>
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<td>150000</td>
</tr>
<tr>
<td>Cd</td>
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</tr>
<tr>
<td>Co</td>
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<td>&lt;5.0</td>
</tr>
<tr>
<td>Cr</td>
<td>32.8</td>
<td>24</td>
</tr>
<tr>
<td>Cu</td>
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<td>12</td>
</tr>
<tr>
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<td>11000</td>
<td>10000</td>
</tr>
<tr>
<td>K**</td>
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<td>2800</td>
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<td>20000</td>
</tr>
<tr>
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</tr>
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<td>&lt;2.0</td>
</tr>
<tr>
<td>Na</td>
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<td>1200</td>
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<tr>
<td>Ni</td>
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<td>9.4</td>
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<tr>
<td>P</td>
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<td>400</td>
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<tr>
<td>Pb</td>
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<td>&lt;10</td>
</tr>
<tr>
<td>S</td>
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<td>Sb</td>
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<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Sn</td>
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<td>20</td>
</tr>
<tr>
<td>Sr</td>
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<td>280</td>
</tr>
<tr>
<td>Ti</td>
<td>1300</td>
<td>1100</td>
</tr>
<tr>
<td>Tl</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>U</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>V</td>
<td>38.9</td>
<td>33</td>
</tr>
<tr>
<td>Zn</td>
<td>79.7</td>
<td>36</td>
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</table>
Appendix D: XRD Results

Figure A-1: XRD results on HCC fines. Quartz, calcite, dolomite, portlandite and rutile were identified as crystalline phases.

Figure A-2: XRD results on HCC coarse. Portlandite, dolomite, calcite, quartz and rutile were identified as crystalline phases.
Figure A-3: XRD results on LCC fine. Quartz, calcite, dolomite, rutile, portlandite, and phlogopite were identified.

Figure A-4: XRD results on LCC coarse. Calcite, dolomite, rutile, phlogopite, quartz and portlandite were identified as crystalline phases.
Figure A-5: XRD results on PCC that was produced from waste concrete by using a HCl:(Ca+Mg) ratio of 0.5:1 and a reaction time of 30 minutes for the precipitation step. Calcite and vaterite were identified as crystalline phases.
Figure A-6: XRD results on PCC made from waste concrete with a HCl:(Ca+Mg) ratio of 0.5:1 and 24 hours of reaction time in the precipitation step. Calcite was the only crystalline CaCO$_3$ polymorph identified.
Figure A-7: XRD results on PCC that was produced from waste concrete by using a HCl:(Ca+Mg) ratio of 2.0:1.0, a purification pH of 9.0 and a reaction time of 30 minutes for the precipitation step. Magnesian calcite was the only crystalline phase identified, however some amorphous content may explain the low angle pattern that lacks defined peaks.
Figure A-8: XRD results on PCC that was produced from waste concrete by using a HCl:(Ca+Mg) ratio of 2.0:1.0, a purification pH of 9.0 and a reaction time of 24 hours for the precipitation step. Magnesian calcite was the only crystalline phase identified, however some amorphous content may explain the low angle pattern that lacks defined peaks.
Figure A-9: XRD results of purification residues that were produced at various pH values after leaching with a HCl:(Ca+Mg) ratio of 2.0. NaOH was added as a purification agent. No crystalline phases were identified with a purification pH of 9.0, 10.0 or 11.0, likely because the solids were completely amorphous. One defined peak was found in the pH 12.0 residue, but was unresolved.
Appendix E: Sieve Fraction Results of Crushed Waste Concrete

Table A-6: Seize results after crushing various types of waste concrete via jaw crusher.

<table>
<thead>
<tr>
<th>particle size (mm)</th>
<th>HCC mass (g)</th>
<th>HCC mass (%)</th>
<th>LCC mass (g)</th>
<th>LCC mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0-5.0</td>
<td>2049.4</td>
<td>38.57</td>
<td>3142.1</td>
<td>37.59</td>
</tr>
<tr>
<td>5-3.327</td>
<td>1193.9</td>
<td>22.47</td>
<td>1856</td>
<td>22.21</td>
</tr>
<tr>
<td>3.327-2.36</td>
<td>450.9</td>
<td>8.49</td>
<td>806.4</td>
<td>9.65</td>
</tr>
<tr>
<td>2.36-1.4</td>
<td>471.6</td>
<td>8.88</td>
<td>783.8</td>
<td>9.38</td>
</tr>
<tr>
<td>1.4-1.0</td>
<td>246.6</td>
<td>4.64</td>
<td>360.5</td>
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</tr>
<tr>
<td>1.0-0.425</td>
<td>421.7</td>
<td>7.94</td>
<td>715.5</td>
<td>8.56</td>
</tr>
<tr>
<td>0.425-0.105</td>
<td>350.9</td>
<td>6.60</td>
<td>541.8</td>
<td>6.48</td>
</tr>
<tr>
<td>&lt;0.105</td>
<td>128.6</td>
<td>2.42</td>
<td>152</td>
<td>1.82</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>5313.6</strong></td>
<td><strong>100</strong></td>
<td><strong>8358.1</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>
Appendix F: Ionic Strength

In electrolyte solutions, each ion will exert an electrostatic force on every other ion, and this force increases as the distance between ions is reduced. The extent of these electrostatic forces are determined by ionic strength ($I$), which is influenced by the ionic concentration ($m$) because higher concentrations reduce the distance between ions, and by the ion charge ($z$). Ionic strength is calculated in units of molality (moles solute/kg solvent) or molarity (moles/L):

$$I = \frac{1}{2} \sum_j m_j z_j^2$$

In a 0.25 M CaCl$_2$ solution, for example, the ionic strength is:

$$I = \frac{1}{2} \left( (0.25 \times 2^2) + (0.5 \times 1^2) \right) = 0.75 \, M$$

The importance of ionic strength is that it influences the solubility of all metals because activity depends on ionic strength. Activity is essentially the “effective concentration” of a species in a mixture and is defined as the concentration ($m$) times the activity coefficient ($\gamma$); concentration is measured, and activity coefficients can be calculated if the ionic strength is known; in idealized solution with no electrostatic forces $\alpha = 1$.

$$\alpha = \gamma m$$

Ionic strength can increase the solubility of a metals because aqueous complexes form (where charges are stuck together, such as FeCl$^+$), and these complexes act as another “stable home” for metals. In other words, ionic strength can decrease the activity coefficient and therefore increase the solubility of metals by decreasing activity. Consider the solubility of Mg(OH)$_2$:

$$\text{Mg(OH)}_2(s) \leftrightarrow \text{Mg}^{2+} + 2\text{OH}^-$$

$$k_{sp} = \alpha_{\text{Mg}^{2+}} \cdot \alpha_{\text{OH}^-}^2 \quad \text{where} \quad \text{pOH} = -\log(\alpha_{\text{OH}^-})$$

$$\alpha_{\text{Mg}^{2+}} = \frac{k_{sp}}{\alpha_{\text{OH}^-}^2}$$
\[
\gamma_{Mg^{2+}} \cdot [Mg^{2+}] = \frac{k_{sp}}{\alpha_{\Delta H^-}}
\]

\[
[Mg^{2+}] = \frac{k_{sp}}{\alpha_{\Delta H^-} \cdot \gamma_{Mg^{2+}}}
\]

Therefore the equilibrium \([Mg^{2+}]\) increases as \(\gamma_{Mg^{2+}}\) decreases.

There are various theoretical models for calculating activity coefficients, two of which are the Debye-Huckel and the Davies equations. White (2013) explained that the Davies equation is slightly more accurate for solutions with an ionic strength between 0.1 and 1.0 M. Davies equation is:

\[
\log_{10} \gamma_i = -A z_i^2 \left( \frac{\sqrt{l}}{1 + \sqrt{l} - bl} \right)
\]

where \(A\) is 0.5092 at 25°C and \(b\) is approximately 0.3 (reviewed in White, 2013). The relationship between the activity coefficient and ionic strength is shown in Figure A-10:

![Figure A-10: The activity coefficients for mono, di, and trivalent ions vs. ionic strength, calculated via Davies equation. The conditions relevant to the experiments in this thesis are shown.](image)

From this figure it can be seen that both the charge of the ion and ionic strength have a significant influence on the activity coefficient. White (2013) explained that the activity coefficients start to increase (i.e. metal solubility decreases) at ionic strengths above
approximately 0.5 M because of the increasing effects of both solvation and ion association. The effect of solvation is where water molecules bind to ions as solvation shells and the water molecules move with the ion as a single entity. These water molecules are unavailable for reaction, and therefore solvation reduces the effective concentration (activity) of water; this increases the activity of the solutes. Ion association can reduce the ionic strength of a solution, and therefore increase activity by reducing the extent of electrostatic interactions among ions; ionic strength is reduced by the formation of ion pairs which form when a positive and negative charge approach closer than a critical distance, and the binding electrostatic energy exceeds twice the repelling thermal energy. When the ions are electrostatically bound the net charge is neutral, hence why the effective ionic strength decreases.

Truesdell and Jones (1974) developed a model to better account for all the effects on activity coefficients at high ionic strength:

\[
\log \gamma_i = \frac{-z_i^2 A \sqrt{I}}{1 + B \tilde{a}_i \sqrt{I}} + b_i l
\]

Where \(A\) and \(B\) are 0.5092 and 0.3283 at 25°C (the same as in the Debye-Huckel model), and parameters \(\tilde{a}\) and \(b\) where empirically determined by Truesedell and Jones to be 5.0 and 0.165 respectively for \(\text{Ca}^{2+}\), and that they vary for each ion (reviewed in White, 2013).

![Figure A-11: The activity coefficient for calcium calculated from the Truesdell and Jones equation at high ionic strengths.](image-url)
Appendix G: The solubility of hydroxides in a CaCl$_2$ solution

The solubility of Ca(OH)$_2$ in water (where $I \approx 0.0$ and $\gamma = 1$, for simplification) can be calculated as follows:

\[
\text{Ca(OH)}_2(s) \leftrightarrow \text{Ca}^{2+} + 2\text{OH}^{-}
\]

\[
\text{K}_{\text{sp}} = \left[\text{Ca}^{2+}\right]\left[\text{OH}^{-}\right]^2
\]

\[
= (x)(2x)^2 = (x)(4x^2) = 4x^3
\]

\[
x = \sqrt[3]{\frac{\text{K}_{\text{sp}}}{4}} = \sqrt[3]{\frac{5.5 \times 10^{-6}}{4}}
\]

\[
= 0.011 \text{ M}
\]

However, the solubility of Ca(OH)$_2$ can be influenced by the common ion effect if CaCl$_2$ is also present in solution because increasing the Ca$^{2+}$ concentration with CaCl$_2$ shifts the equilibrium to the solid state.

The solubility of Ca(OH)$_2$ as a function of CaCl$_2$ concentration can be calculated as follows:

<table>
<thead>
<tr>
<th></th>
<th>Ca$^{2+}$</th>
<th>2OH$^{-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>M</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>+x</td>
<td>+2x</td>
</tr>
<tr>
<td>equilibrium</td>
<td>M+x</td>
<td>2x</td>
</tr>
</tbody>
</table>

\[
\text{K}_{\text{sp}} = \left[\text{Ca}^{2+}\right]\left[\text{OH}^{-}\right]^2
\]

\[
\text{K}_{\text{sp}} = (M+x)(2x)^2
\]

For simplification (M+x) can be reduced to M because x is at most 0.011 M, and the M values ([$\text{CaCl}_2$]) of interest are $\geq 0.25$ M:

\[
\text{K}_{\text{sp}} \approx (M)(2x)^2
\]

\[
\text{K}_{\text{sp}} = 4x^2M
\]
\[ x = \sqrt{\frac{K_{sp}}{4M}} = \sqrt{\frac{5.5 \times 10^{-6}}{4 \times [CaCl_2]}} \]

Since the activity of Ca\(^{2+}\) from the CaCl\(_2\) is of interest rather than concentration, and \(a_{Ca^{2+}} = \gamma_{Ca^{2+}}[CaCl_2]\)

\[ x = \sqrt{\frac{5.5 \times 10^{-6}}{4 \times (\gamma_{Ca^{2+}}[CaCl_2])}} \]

where \(\gamma_{Ca^{2+}}\) depends on ionic strength, i.e. the [CaCl\(_2\)]

Figure A-12: The solubility of calcium hydroxide vs. the concentration of calcium chloride. The \(\gamma_{Ca^{2+}}\) at 0.25 M CaCl\(_2\) was calculated from Davies equation, and from the Truesdell and Jones equation above 0.25 M CaCl\(_2\).

If Ca(OH)\(_2\) is the only significant source of alkalinity, then the pH of a CaCl\(_2\) solution that is saturated with respect to Ca(OH)\(_2\) can also be calculated as:

\[ pOH = -\log(2[Ca(OH)_2]) \]

As an example, the solubility of Ca(OH)\(_2\) in a 0.25 M CaCl\(_2\) solution can be taken from Figure A-12 to calculate the saturation pH:

\[ -\log(2[0.004107452]) = 2.085 \]

\[ pH = 14 - pOH = 14 - 2.085 = 11.91 \]
Therefore the purification pH of this solution exceeds 11.91, then Ca(OH)\(_2\) can be expected to precipitate.

Finally, the solubility of Ca(OH)\(_2\) in 0.25 M CaCl\(_2\) can be calculated as a function of pH as follows:

\[
K_{sp} = [Ca^{2+}][OH^-]^2 \quad \text{let} \quad x = [OH^-]
\]

\[
K_{sp} = [0.5x + 0.25][x]^2 \quad \text{since for every OH}^- \text{ there are 0.5Ca}^{2+}
\]

Now by taking this equation and adding OH\(^-\) to alter the initial pH of the solution we get:

\[
K_{sp} = [0.5x + 0.25][x+y]^2 \quad \text{where} \quad y \quad \text{OH}^- \text{ added to adjust the pH}
\]

Since 0.5\(x\) is equal to the concentration of calcium associated with dissolved Ca(OH)\(_2\), we can rearrange the formula above to:

\[
0.5x = \frac{K_{sp}}{[x+y]^2} - 0.25
\]

However the activity of the Ca\(^{2+}\) from the 0.25 M CaCl\(_2\) will influence the solubility of Ca(OH)\(_2\), so:

\[
0.5x = \frac{K_{sp}}{[x+y]^2} - (\gamma_{Ca^{2+}})(0.25)
\]

\[
\gamma_{Ca^{2+}} = 0.326 \quad \text{(from Figure 1)}
\]

\[
0.5x = \frac{K_{sp}}{[x+y]^2} - (0.326)(0.25)
\]

\[
0.5x = \frac{K_{sp}}{[x+y]^2} - (0.0815)
\]

\[
Ca^{2+}_{Ca(OH)2} = \frac{K_{sp}}{[x+y]^2} - (0.0815)
\]

Then since \(x+y\) is equal to the total [OH\(^-\)], we can produce a graph of the solubility of Ca(OH)\(_2\) in a CaCl\(_2\) solution vs. pH and compare it to the solubility of Ca(OH)\(_2\) in water.
Figure A-13: The solubility of Ca(OH)$_2$ in CaCl$_2$ solutions vs. pH.

The solubility of other metal hydroxides vs. pH in a 0.25 M CaCl$_2$ solution (i.e. where ionic strength = 0.75 M) can be calculated as:

$$Me(OH)_2(s) \leftrightarrow Me^{2+} + 2OH^-$$

$$k_{sp} = \alpha_{Me^{2+}} \cdot \alpha_{OH}^2$$

$$\alpha_{Me^{2+}} = \frac{k_{sp}}{\alpha_{OH}^2}$$

$$\gamma_{Me^{2+}} \cdot [Me^{2+}] = \frac{k_{sp}}{\alpha_{OH}^2}$$

$$[Me^{2+}] = \frac{k_{sp}}{\alpha_{OH}^2 \cdot \gamma_{Me^{2+}}}$$

where pOH = -log($\alpha_{OH}$) and $\gamma_{Me^{2+}}$ = 0.326 when $I$ = 0.75 M

For the hydroxides of trivalent cations the equations becomes:

$$[Me^{3+}] = \frac{k_{sp}}{\alpha_{OH}^3 \cdot \gamma_{Me^{3+}}}$$

Where $\gamma_{Me^{3+}}$ = 0.0802 when $I$ = 0.75 M
Appendix H: Purity and Hydroxide Solubility Calculations

If a target PCC purity of 98.5% CaCO$_3$ and 0.6% MgCO$_3$ is set (similar to that of competing products), then the required molar ratio of Ca:Mg can be calculated to be approximately 140:1. If no silicon is present in solution, then to obtain such a molar ratio prior to precipitation, a target pH of 10.00 can be calculated if it assumed that [CaCl$_2$] = 0.25 M, $\gamma_{Mg^{2+}} = 1$, and that the magnesium concentration is solely controlled by the solubility of Mg(OH)$_2$, and that Ca(OH)$_2$ will not precipitate at pH ≤ 10.00.

$$\frac{[Ca^{2+}]}{[Mg^{2+}]} = 140; \ [Mg^{2+}] = \frac{[Ca^{2+}]}{140}$$

$$[Mg^{2+}] = \frac{k_{sp}}{[OH^-]^2}; \ k_{sp} = 1.8 \times 10^{-11}$$

$$[OH^-] = \sqrt{\frac{k_{sp}}{[Mg^{2+}]/140}}$$

$$[OH^-] = 1.0 \times 10^{-4} \text{ M; pH} = 10.00 \text{ (when [Ca$^{2+}$] = 0.25 M)}$$

However, when ionic strength is accounted for $\gamma_{Mg^{2+}} = 0.326$ and the new target pH is 10.25:

$$[OH^-] = \sqrt{\frac{k_{sp}}{[Mg^{2+}][CaCl_2]/140}}$$

$$[OH^-] = 1.758 \times 10^{-4} \text{ M; pH} = 10.25$$
Assuming that all of the carbonate minerals were dissolved by aqua regia, it appears as though the interpretation that the mass loss in the TGA curve from 450-600°C is CO₂ loss from amorphous/finely crystalline carbonates is not correct in this case. This is because from the Table below it can be seen that the interpreted moles of CO₂/100 g significantly exceeds the moles of calcium + magnesium for one of the size fractions from the high carbonate concrete. Since that is not reasonable, the mass loss between 450-600°C will be unexplained for now, and the mass loss between 600-800°C will be interpreted to be due to CO₂ sublimation.

### Table A-7: Cross checking TGA results with ICP-OES results assess possible identities of unknown thermal decomposition phases.

<table>
<thead>
<tr>
<th>Analytical Method</th>
<th>Low Carbonate Concrete (LCC)</th>
<th>High Carbonate Concrete (HCC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt.%</td>
<td>Dp&lt;105μm</td>
</tr>
<tr>
<td>ICP-OES + aqua regia digestion</td>
<td>Ca</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Ca:Mg molar ratio</td>
<td>3.7:1</td>
</tr>
<tr>
<td>TGA (450-750°C)</td>
<td>CO₂</td>
<td>12.26</td>
</tr>
<tr>
<td></td>
<td>σ CO₂</td>
<td>0.23</td>
</tr>
<tr>
<td>TGA (375-450°C)</td>
<td>Ca(OH)₂</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>σ Ca(OH)₂</td>
<td>0.032</td>
</tr>
<tr>
<td>Moles Mg/100g</td>
<td>0.115202633</td>
<td>0.082287595</td>
</tr>
<tr>
<td>Moles Ca/100g</td>
<td>0.424172863</td>
<td>0.374270173</td>
</tr>
<tr>
<td>Moles CO₂/100g</td>
<td>0.278573052</td>
<td>0.214951147</td>
</tr>
<tr>
<td>% of Ca uncarbonated</td>
<td>61.48494337</td>
<td>64.55406767</td>
</tr>
<tr>
<td>% of Ca as Ca(OH)₂</td>
<td>13.34820983</td>
<td>9.343746878</td>
</tr>
</tbody>
</table>
Figure A-14: The extraction yield of various elements from different materials v.s. the 
HCl:(Ca+Mg) ratio. The legend in Figure 4.4 (a) applies to these graphs as well, and the Ca:Mg 
ratio applies to the description of each material. 15.0g of waste concrete fines and various volumes 
of 0.5 M HCl were used, the solutions were stirred at 400rpm for 120 minutes before sampling.
Figure A-15: SEM images of PCC produced with a HCl:(Ca+Mg) ratio of 2.0 and a purification pH of 9.0 after 30 minutes (left) and 24 hours (right) of reaction time.

Figure A-16: EDAX of PCC produced with a HCl:(Ca+Mg) ratio of 2.0 and a purification pH of 9.0.
Figure A-17: Interpretation of purification residues produced at various purification pH values via NaOH addition. HCl:(Ca+Mg) =2.0 with low carbonate concrete. Constructed by measuring the mass of the residues and EDAX analysis of the solids. All residues were entirely amorphous phases (Appendix D), except the residue at pH 12.0 had one unidentified crystalline phase.
Appendix J Sulphate-Sulphide pe vs. pH Calculations

The pe vs. pH plot for the sulphate-sulphide system was constructed following the general procedure for pe vs. pH diagrams from White (2013) and half-cell Equations I-IV.

Table: Free energies of formation of various sulphur species (White, 2013, p. 114). Values are in kJ/mol, standard state is 25°C and 0.1 MPA.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G^0$</th>
<th>Species</th>
<th>$\Delta G^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^{2-}$ (aq)</td>
<td>+85.81</td>
<td>$SO_4^{2-}$ (aq)</td>
<td>-744.54</td>
</tr>
<tr>
<td>HS (aq)</td>
<td>+12.09</td>
<td>HSO$_4^-$ (aq)</td>
<td>-755.92</td>
</tr>
<tr>
<td>H$_2$S (aq)</td>
<td>-27.82</td>
<td>H$_2$O</td>
<td>-237.19</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0</td>
<td>H$_2$ (g)</td>
<td>0</td>
</tr>
<tr>
<td>O$_2$ (g)</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Examples of the half-cell equations used:

I) $SO_4^{2-} + 8H^+ + 8e^- \leftrightarrow S^{2-} + 4H_2O \quad \Delta G = -118.41 \text{ kJ/mol}$

II) $SO_4^{2-} + 10H^+ + 8e^- \leftrightarrow H_2S + 4H_2O \quad \Delta G = -232.04 \text{ kJ/mol}$

III) $SO_4^{2-} + 9H^+ + 8e^- \leftrightarrow HS^- + 4H_2O \quad \Delta G = -192.13 \text{ kJ/mol}$

IV) $HSO_4^- + 9H^+ + 8e^- \leftrightarrow H_2S + 4H_2O \quad \Delta G = -220.66 \text{ kJ/mol}$

Example Calculation with Equation I:

$$ \log K = \frac{-\Delta G}{2.3RT} \quad \log K = 20.8 $$

Where $R = 8.314 \text{ J/mol} \text{ and } T = 298.15 \text{ K}$

$$ K = \frac{\alpha_{S^{2-}}\alpha_{H_2O}^4}{\alpha_{SO_4^{2-}}^8\alpha_{H^+}^8\alpha_{e^-}^8} $$

$$ K = \log(\alpha_{S^{2-}}) + 4\log(\alpha_{H_2O}^4) - \log(\alpha_{SO_4^{2-}}^8) + 8pH + 8pe $$

Because pH = $-\log(\alpha_{H^+})$ and pe = $-\log(\alpha_{e^-})$

$$ \log K = \log \left(\frac{\alpha_{S^{2-}}}{\alpha_{SO_4^{2-}}^8}\right) + 8pH + 8pe $$

Since the boundary between the two species is defined by where $\alpha_{S^{2-}} = \alpha_{SO_4^{2-}}$

$$ pe = 2.6 - pH $$
Annex I: Supplementary Information on Recycled Aggregate Performance

Source: Tam et al. (2007)

<table>
<thead>
<tr>
<th>Source(s)</th>
<th>Replacement ratio</th>
<th>Compressive strength</th>
<th>Flexural strength</th>
<th>Modulus of elasticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acker (1998)</td>
<td>100% replacement of coarse recycled aggregate (CRRA)</td>
<td>17.2% lower</td>
<td>20% lower</td>
<td>23% lower</td>
</tr>
<tr>
<td>Ahmed and Strible (1995)</td>
<td>100% replacement of CRA</td>
<td>33% lower</td>
<td>16% lower</td>
<td>(at 14 days)</td>
</tr>
<tr>
<td>Betschneider (2004)</td>
<td>100% replacement of CRA</td>
<td>8.1% lower</td>
<td>8.1% lower</td>
<td>5.8% lower</td>
</tr>
<tr>
<td>Frondistrou-Vassas (1977)</td>
<td>100% replacement of CRA</td>
<td>4.14% lower</td>
<td>40% lower</td>
<td></td>
</tr>
<tr>
<td>Gubbi et al. (2004)</td>
<td>100% replacement of CRA</td>
<td>75% replacement of CRA</td>
<td>28.3% lower</td>
<td></td>
</tr>
<tr>
<td>Hassen and Marga (1988)</td>
<td>100% replacement of CRA</td>
<td>30% lower</td>
<td>30% lower</td>
<td>30% lower</td>
</tr>
<tr>
<td>Ikeda et al. (1988)</td>
<td>100% replacement of CRA</td>
<td>40% lower</td>
<td>40% lower</td>
<td></td>
</tr>
<tr>
<td>Kakizaki et al. (1988)</td>
<td>100% replacement of CRA and fine recycled aggregate (FRA)</td>
<td>32% lower</td>
<td>32% lower</td>
<td></td>
</tr>
<tr>
<td>Masood et al. (2001)</td>
<td>10% replacement of FRA</td>
<td>20% lower</td>
<td>22.6% lower</td>
<td>22.7% lower</td>
</tr>
<tr>
<td>Nishiyabashi and Yamura (1983)</td>
<td>100% replacement of CRA</td>
<td>15–30% lower</td>
<td>15% lower</td>
<td></td>
</tr>
<tr>
<td>Roos (2003)</td>
<td>100% replacement of CRA</td>
<td>34% lower</td>
<td>36% lower</td>
<td></td>
</tr>
<tr>
<td>Toranishi et al. (1998)</td>
<td>50% replacement of CRA</td>
<td>57.3% lower</td>
<td>30.5% lower</td>
<td></td>
</tr>
<tr>
<td>Topcu (1997)</td>
<td>30% replacement of CRA</td>
<td>31.8% lower</td>
<td>45.5% lower</td>
<td></td>
</tr>
<tr>
<td>Yangi et al. (1993)</td>
<td>30% replacement of CRA</td>
<td>0.3–11.2% lower</td>
<td>0–18.7% lower</td>
<td></td>
</tr>
<tr>
<td>50% replacement of CRA</td>
<td>1.2–16.8% lower</td>
<td>2.8–25.1% lower</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% replacement of CRA</td>
<td>4.1–19.7% lower</td>
<td>1.1–25.8% lower</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tests are conducted in the curing of 28 days.

The quality of these recycled aggregates is poor, with water absorption of 7% in 30 min.

Table 2b: Summary on the previous researches on RAC

<table>
<thead>
<tr>
<th>Source(s)</th>
<th>Replacement ratio</th>
<th>Compressive strength</th>
<th>Flexural strength</th>
<th>Modulus of elasticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yangi et al. (1993)</td>
<td>30% replacement of CRA</td>
<td>0.3–11.2% lower</td>
<td>0–18.7% lower</td>
<td></td>
</tr>
<tr>
<td>50% replacement of CRA</td>
<td>1.2–16.8% lower</td>
<td>2.8–25.1% lower</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% replacement of CRA</td>
<td>4.1–19.7% lower</td>
<td>1.1–25.8% lower</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reuse of demolished concrete (Kawano, 1995)

Demolished member: Man-made reef, paving stone

<table>
<thead>
<tr>
<th>Broken into 20–40 cm</th>
<th>Protection of levee</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crushed (~50 mm)</td>
<td>Sub-base, backfilling, foundation materials</td>
</tr>
<tr>
<td>Crushed and worn (~40 mm)</td>
<td>Concrete and asphalt concrete aggregate sub-base material, backfilling material</td>
</tr>
<tr>
<td>Powder (by-product through crushing)</td>
<td>Filler for asphalt concrete, soil stabilization materials</td>
</tr>
</tbody>
</table>