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공학박사학위논문

**Comparison of Various
Extractants for Mineral
Carbonation of Industrial Wastes**

추출제에 따른 산업부산물
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에너지시스템공학부

문명욱

Abstract

Comparison of Various Extractants for Mineral Carbonation of Industrial Wastes

Myoungwook Mun

Department of Energy Systems Engineering

The Graduate School

Seoul National University

When considering domestic conditions in Korea, one suitable technology for carbon sequestration is mineral carbonation. Research is still in its infancy, although many studies have been conducted to investigate various ways of enhancing the carbonation reaction.

In this study, blast furnace slag and waste cement were reacted with various acids at the same concentration (0.1 M) under atmospheric conditions, in order to determine their efficiency for mineral carbonation. Hydrochloric acid, acetic acid, oxalic acid, citric acid, EDTA, and ammonium chloride were used as extractants. Based on maximum calcium concentration (2400 mg/L) and selectivity (99%), waste cement reacted better with acids, including EDTA, than slag. This is attributed to the greater

specific surface area (porous structure) of cement. Use of EDTA improved extraction ability, but could not reduce usage of caustic reagent in during the carbonation step. Organic acids (oxalic acid and citric acid) had little effect on dissolution. Subsequently, calcium-rich solutions from each type of wastes were reacted with 99.9% CO₂ to precipitate calcium carbonate. The solid product obtained from waste cement was white and in the form of uniform particles (under 3 μm), i.e., pure calcite, without other elements. In contrast, the product from slag had light brown and heterogeneous particles of lower quality, mainly due to the presence of silicates and aluminates.

Based on these results, waste cement was selected as a suitable material for mineral carbonation, and further experiments were conducted with hydrochloric acid, acetic acid, and ammonium chloride as effective extractants. At low acid concentrations (0.1M), the concentration of calcium was similar regardless of acid type. Increasing acid concentration resulted in a linear relationship with the maximum ratio of calcium extraction, but the ratio of increment depended on the type of acid. Although the yield of calcium extracted with NH₄Cl was lower than that extracted with HCl and CH₃COOH, vaterite was precipitated without introducing a basic reagent into carbonation. Moreover, the NH₄Cl regenerated during carbonation can be reused for calcium extraction. However, test results using regenerated

NH₄Cl solution in a cyclical fashion revealed that the process was not perfectly cyclical, but rather the calcium content increased after each precipitation step as the cycle proceeded. It may be necessary to remove residual calcium ions for complete recycling. However, such properties of ammonium chloride indicate that it is a very economical extraction agent compared to other acids. In addition, direct carbonation of synthetic flue gas resulted in greater efficiency, by reducing costs that would otherwise be involved in the carbon capture process.

The reaction of waste cement and acids was analyzed using PHREEQC, a geochemical computer program. The simulation was based on thermodynamic equilibrium. Even though the initial pH of CH₃COOH was higher than that of HCl for dissociation constants, the equilibrium pH and calcium concentration of extraction solution were similar for the two acids. NH₄Cl showed a lower extraction rate, except at 0.1 M. These results were similar to those obtained experimentally. Calcium was present at 93%, which was almost all in Ca²⁺ form, with some in the form of CaOH⁺. S was mainly found as SO₄²⁻ and CaSO₄, Al was found as Al(OH)₄ and Al(OH)₃, and Si was present as H₃SiO₄⁻ and H₄SiO₄. Main species of all elements were the same in the Eh-pH diagram. In a periodic fashion, the amount of calcium in the NH₄Cl solution fluctuated within specific values, unlike experimental

results for calcium accumulation in the extraction solution. There are two possible reasons for these deviations: (1) kinetics, and (2) lack of thermodynamic data for the formation of different types of calcium carbonate polymorphs, with the latter requiring further study. One reason was the kinetic/thermodynamic balance controlled by the amount of Ca^{2+} and CO_2 present in the solution, which may explain the observed vaterite formations. However, the kinetic aspect was not considered in this simulation and, may be responsible for the discrepancy between simulated and experimental results. However, it is feasible to use the geochemical model to evaluate the mineral carbonation process with correction factors since the variation between experimental and simulation results remained reasonably constant throughout the test cycle.

Key words: Mineral carbonation, Waste cement, Blast furnace slag, Ammonium chloride, Thermodynamic modeling

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Chapter 1 Introduction

1.1. Issues

Annual carbon dioxide emissions from fossil fuel combustion amounted to 9.5 [8.7–10.3] GtC/yr in 2011, 54% more than 1990 levels (IPCC Fifth Assessment Report, 2014). Of the various greenhouse gases, carbon dioxide is the largest contribution to the enhanced greenhouse effect. Global average surface temperature has increased by 0.78 °C, likely to be the largest increase in temperature over the last millennium. It is possible that global warming could cause changes in natural ecosystems, leading to massive losses of biodiversity and ecosystem functions.

In order to prevent such devastating consequences from climate change, anthropogenic CO₂ emissions should be considerably reduced. Three major actions for reducing CO₂ emissions can be distinguished: (1) reduction of energy consumption to maximize the efficiency of facilities, (2) energy generation from non-fossil sources without CO₂ emissions, and (3) carbon capture and storage (CCS). Although energy-saving technologies can be relatively easily applied (in comparison with other technologies), there are a number of limitations to achieving significant CO₂ reductions. Alternative

energy sources may prove to be the ultimate energy sources for humanity, but these are difficult to utilize in the short term. The application of carbon capture and storage (CCS) technologies is therefore considered to be the most practical option at present for stabilizing the concentration of atmospheric CO₂.

CCS technology involves capturing CO₂ produced by large industrial plants, compressing it for transportation, and then injecting it deep into a rock formation at a carefully selected and safe site, where it is permanently stored.

Because CCS can achieve significant CO₂ emission reductions, it is considered a key option within the portfolio of approaches required to reduce greenhouse gas emissions. Consequently, a large number of CCS projects underway around the world. However, their integration into a single process is challenging and has yet to be demonstrated. Moreover, the expected progress has not been made in the deployment of geological storage due to delays in implementing some large demonstration projects (e.g. Mongstad in Norway) due to higher complexity than expected, as well as due to general public acceptance issues related to potential leakages and surface transport of supercritical CO₂. Overall, CO₂ geological storage involves a great deal of uncertainty in terms of quantification of storage potential, monitoring of

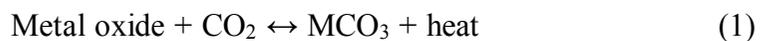
injected CO₂, and engineering challenges to ensure that injected CO₂ remains in the subsurface for hundreds or thousands of years.

In this scenario, Mineral Carbonation (MC) represents an alternative CCS option, which may be particularly suitable for small sources, where geological sequestration is not viable.

1.2. Mineral carbonation

MC is based on natural weathering of silicate rocks and is an alternative to CO₂ sequestration. It has been used in small countries since the 1990s (Seifritz, 1990). In weathering processes, rocks containing alkali and alkaline earth elements (e.g., Na, K, Ca, and Mg) react with rainwater saturated with dissolved atmospheric CO₂ to form carbonate minerals. However, applying the weathering process in industry represents a major challenge, because the reaction rate is extremely slow. If this could be enhanced, it could replace gaseous carbon dioxide with solid carbonates.

MC employs a basic concept to produce carbonate minerals by reacting carbon dioxide with minerals mainly composed of calcium or magnesium, via the following reaction:



Since carbonate represents the lowest energy-state of carbon, the reaction is exothermic and thermo-dynamically favored at low temperatures (Lackner et al., 1995). The amount of heat depends on the specific metal and on the material containing the metal oxide.

In addition to the use of natural minerals as a feedstock for CO₂ sequestration, industrial waste sources (such as slags and coal ashes) might also be used for this purpose. Figure 1-1 provides a schematic drawing of MC based on both mineral and waste carbonation. A by-product could be used for mine reclamation and beneficially reused or disposed of.

Compared to other carbon dioxide storage routes, MC has the benefit of being environmentally benign and of providing virtually permanent trapping of carbon dioxide in the form of carbonate minerals. Another benefit is that, unlike geological sequestration routes, it provides long-term sequestration without the need for post-monitoring once the carbon dioxide has been fixed (Metz et al., 2005). The third benefit is that this approach has the largest potential capacity for CO₂ sequestration for storage in various forms when CO₂ is reacted with magnesium-based silicates, which are abundant around the world (Lackner et al., 1995).

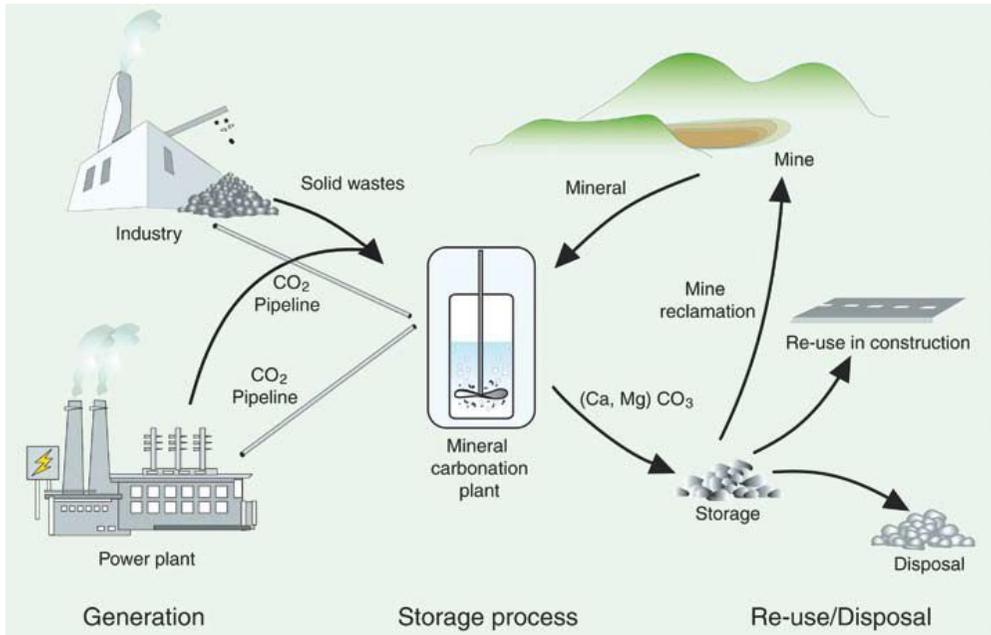


Figure 1-1. Material flux and process steps associated with mineral carbonation of silicate rocks or industrial residues. (Metz et al., 2005)

According to literature analyzing the maturity and cost of CCS technologies, MC is still in its early research phase, even though there have been many studies investigating various ways of enhancing carbonation. In addition, the cost of sequestering a ton of CO₂ by mineralization is about 50–100 US\$, which is excessive compared to the other sequestration options shown in Table 1-1.

Table 1-1. Estimates of CO₂ storage costs. (Metz et al., 2005)

Option	Representative Cost Range (US\$/ton CO₂ stored)	Representative Cost Range (US\$/ton C stored)
<hr/>		
Geological		
Storage	0.5–8.0	2–29
Monitoring	0.1–0.3	0.4–1.1
<hr/>		
Ocean		
Pipeline	6–31	22–114
Ship (Platform or Moving Ship Injection)	12–16	44–59
<hr/>		
Mineral Carbonation	50–100	180–370
<hr/>		

Although exploration and verification of storage candidate sites for geological storage had not been seriously undertaken until recently, the potential amount of domestic CO₂ storage is known to be about 250 Mt. This is insufficient to deal with CO₂ emissions that were expected to reach about 640 Mt as early as 2012 (Kang, 2009). Processes by which to transfer captured CO₂ abroad have therefore also been studied (Takagi, 2007). If a

location in Australia is designated as a candidate storage site in the next generation CCS model of Korea, it is expected that CO₂ transport would only be allowed via shipping. In this case, the cost of transport, in accordance with distance, would be 30 to 60 US\$ per CO₂ ton, if the distance between Korea and Australia is estimated at 5,000–8,000km (Han et al., 2011). Considering this situation, there is a need to develop MC as a technical alternative in order to achieve the targets set in the Korean national strategy for CO₂.

1.3. Comparison of carbonation and geological storage

Even if storage costs for MC are high, it has advantages over geological storage (see Table 1-2 for a full comparison). In the case of geological storage, there is a need for large-scale initial investment such as specification and transport of CO₂, exploration of storage areas, and monitoring. In this case, carbon dioxide is considered as waste to be treated. On the other hand, MC is expected to occur over a relatively short period, because it requires much less development and industrial infrastructure than that required for geological storage. In this case, carbon dioxide is regarded as a raw material that could provide additional benefits and reduced

processing costs. If there is further consideration of the cost reductions associated with industrial waste processing and with the creation of profit from use of high-value carbonate, this option will become economical. Calcium carbonates, in particular, have much wider uses than magnesium carbonates in construction, chemistry, metallurgy and agriculture (Zevenhoven et al., 2006). Calcium carbonate is increasingly used in the pulp and paper industry as a paper filler (instead of clay) and in coatings to provide opacity, high brightness, and improved printability (because of its good ink receptivity) (Hase et al., 1998).

Table 1-2. Comparison of the technologies of CO₂ geological storage and mineral carbonation. (Han et al., 2011)

Category	Geological Storage	Mineral Carbonation
Specification	- Purity > 95%	
	- H ₂ O removal for inhibition of hydrates	- No specific purity requirement.
	- Removal of impurities	- Use flue gas without CO ₂ capture
Transport	Major factor: distance	Relatively low transportation cost
Storage	- Large initial investment cost	- Small initial investment cost
	- Geology- or country-specific option: limits the technology's application	- Pre-treatment of raw materials - Various raw materials
Technology/ Reaction	- Long-term & slow carbonation reaction	- Acceleration of carbonation: additional energy required
	- Large investment for high pressure injection	- Initial investment for carbonation
Capacity	Large scale	Medium or small scale
Monitoring &Verification	- Long-term investigation of leakage	- No need for monitoring
	- Safety verification needed	- Environmentally benign
By-products	Impossible to reuse	Possible to reuse as valuable products
Legal/Public Issues	Needs public acceptance	Needs new regulations for waste disposal

1.4. Research trends abroad

There has been active research on MC in the USA, Finland, and Japan. In the United States, substantial research has been conducted at LANL (Los Alamos National Laboratory, New Mexico), NETL (National Energy Technology Laboratory in Oregon), at the Albany Research Center (Oregon), and at Columbia University (New York). Finland has developed technology that supplies energy required from the heat of the carbonation reaction, with this work conducted at Åbo Akademi University and at the Helsinki University of Technology. In Japan, studies of MC using industrial waste (such as waste concrete) have been conducted at Tokyo University. Although many studies have investigated various ways to enhance indirect carbonation, the process is still too expensive to be applied on a larger scale.

USA. The focus of CCS research was initially geological storage in relation to enhanced oil recovery (Enhanced Oil Recovery, EOR). However, research on MC started in the late 1990s. Research has mainly involve natural minerals (such as olivine and serpentine) and has been conducted in relation to geographical conditions (Blencoe et al., 2003). In addition, direct carbonation has been studied, using carbon, aqueous carbonation, and carbonation with supercritical CO₂. However, there have been difficulties in

developing economic processes due to the problem of inadequate reactivity of Mg. In addition, although limited, there has also been some research using industrial residues (Stolaroff et al., 2005). Although the American Iron & Steel Institute has an ongoing CO₂ Breakthrough Program aimed at reductions, MC was not on the government's roadmap, and it is difficult to conduct research without adequate funding. In the near future, active research may become possible after re-evaluation of this situation, because there is still interest in the field.

Europe. Finland and the Netherlands in Europe started focusing on research related to MC in the 2000s (Huijgen, 2006).

In Finland, which developed carbonation using natural minerals and steel slag, some research has been funded by government. MC research was mainly focused on the use of the serpentine mined in nickel or copper mines. Carbonation of serpentine was expected to be able to dispose of 2-Gt CO₂ (Teir, 2008). It was determined that slag carbonation could be competitive with production of synthetic calcium carbonate, and this provided the advantage of processing over one million tons of steel slag. Although early research was carried out using acetic acid to extract calcium and achieve carbonation, more recently a variety of acids (e.g., sulfuric and nitric acids),

ammonium salts, and ammonium nitrate have been used for extraction, due to economic problems (Eloneva et al., 2008).

In the Netherlands, Enhanced Coal-Bed Methane was studied around 2000. Soon after, specific research was carried out to determine the potential storage capacity of CO₂, and technical and economic feasibility in areas such as Peel, Zuid Limburg and Achterhoek (Hamelinck et al., 2002). In addition, in 2004, 100 tCO₂/day were injected for EOR during a K12B project (IPCC Special Report, 2005). At the same time, research on MC using industrial waste was conducted at ECN (Energy Research Centre of the Netherlands), with the aim of improving the environment by altering the physical properties of steel slag to reduce contaminant leaching (Huijgen, 2006). At this time, there appears to be no clear policy involving MC planned in either the Netherlands or the EU.

Japan. CCS was considered a key element in the carbon dioxide technology map. MC was addressed using chemical conversion technology to effectively use CO₂ via several scenarios for technology deployment. For example, RITE (Research Institute of Innovative Technology for the Earth) used ammonium chloride in a carbonation study of concrete and steel slag in the mid-2000s (Yogo et al., 2008). There was a concentrated effort at Tokyo

University with potential applications in industry (Kakizawa et al., 2001). In addition, there was a recent pilot study involving carbonation technology (Nippon Concrete Industries Co. Ltd.) conducted using concrete sludge.

1.5. Domestic research trends

Most government officials and researchers in Korea regard geological storage as the primary CCS technology due to the relatively large storage capacity afforded by this option, and due to the existence of demonstration facilities. Although national CCS research started around 2000, at that time it was focused on research related to capture and studies related to storage were therefore not considered important. The level of domestic research into CO₂ storage using MC was, in particular, very weak compared to that in more developed countries. Limited laboratory studies of domestic MC have been conducted. Although such studies began in earnest at the Korea Institute of Geoscience and Mineral Resources (KIGAM) after the mid-2000s, only preliminary studies or internal research have been conducted until recently.

Research conducted on carbonation using steel slag can be considered to constitute the first domestic study. In this study, rather than focus on MC, the main purpose was to ensure the environmental stability of steelmaking

slag to be used as an aggregate after reaction with CO₂. In 2009, research was conducted relating to stabilization of harmful heavy metals in various wastes and CO₂ utilization technology, and a comprehensive processing pilot plant for recycling public waste using CO₂ was constructed by KIGAM (Trend of Technology report by Korea Environmental Industry & Technology Institute, 2010).

According to the project report of the Korea Institute of Geoscience and Mineral Resources, domestic MC using natural minerals was at a level of about 30% compared to developed countries, but research using industrial wastes (and related developments), was still lacking (Research report by Ministry of Environment, 2009). However, there is sufficient technological development, when considering that there is presently no particular global technical superiority, and there is therefore less of a technological gap with respect to developed countries.

1.6. Research purpose

Carbonation is already a well-known technology, but a great deal of research is necessary to secure cost-effective core technologies. To achieve this, there need to be investigations into the development of quick, cost-

effective methods for combining carbon dioxide with magnesium or calcium compounds from rock or from alkaline industrial wastes.

Various attempts to speed up carbonation include the use of both dry and wet methods, additives, heating and pressurizing the reactor, dividing the process into multiple steps, and pretreatment of the mineral source. Two main types of routes can be distinguished: (i) direct carbonation and (ii) indirect carbonation (Figure 1-2).

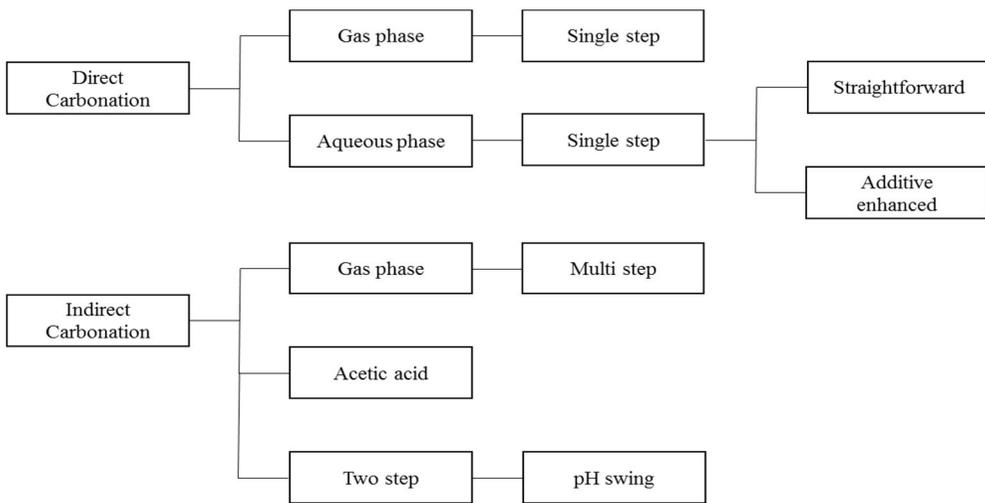


Figure 1-2. Main carbonation processes and variants. (Sipilä et al., 2008)

Although direct carbonation has been extensively investigated by a number of laboratories, most of these processes produce an aqueous slurry mixed with other by-products, from which it is difficult to separate

carbonates (O'Connor et al., 2005). Indirect processes allow separation of silica or other by-products, such as metals and minerals, before the carbonation step (Kakizawa et al., 2001). Indirect carbonation is therefore a better alternative for producing separate streams of carbonates and other materials for further recovery. However, MC, in general, is considered to be more expensive compared to geological storage options, mainly due to the cost and energy involved in pre-treatment, such as fine grinding and extraction of Mg and Ca from source minerals.

Especially in the case of indirect carbonation, excess acid is required to achieve high extraction efficiency, and in turn, the pH of the extraction solution can be very low (Lackne et al., 1995, Goff et al., 1998). This results in unfavorable conditions for the subsequent carbonation reaction, which favors basic pH conditions. It is therefore necessary to raise the pH before carbonation. If a caustic reagent is used for this purpose, a considerable quantity of reagents would be required for the extraction and carbonation step. Alternately, organic acids such as EDTA can be added to enhance the dissolution of alkaline metals from silicates under mild acid conditions (Park et al., 2003). This would reduce the usage of caustic reagents during the second step. However, organic acid is very expensive and its use renders it more difficult to recover and recycle acid used in the leaching step. Another

approach towards reduction of energy and acid consumption is the use of acetic acid. The main advantage is use of a less severe extraction medium and the ability to recover acetic acid during the second step (Kakizawa, et al., 2001, Teir, et al., 2007).

There have been several other attempts to develop a process with full chemical recycling. Kodama et al. developed a process that uses NH_4Cl as an extracting agent (Kodama et al., 2008). It was reported that NH_4Cl could dissolve calcium ions efficiently and selectively from slag. After removing slag residue, injection of CO_2 into the leaching solution resulted in the precipitation of pure calcium carbonate and NH_4Cl was regenerated as carbonation proceeded. A caustic reagent was not required for carbonation in this process as the solution pH was stabilized in the alkaline region during extraction. This process seems to be the most promising given the potential for reagent recovery and reuse. This study therefore investigated this process as a preferential method for CO_2 sequestration.

There are a number of potentially suitable industrial wastes that are generated in large quantities in Korea, including slag, coal fly ash, and waste concrete. In Korea, over 20 million tons of steel slag are generated each year. Since the calcium content of typical slag is over 40 wt%, this material has great potential for use in the CO_2 sequestration process. However, this

material contains many potentially hazardous heavy metals that can be leached out during extraction. This could complicate the process and the resulting carbonated products may not be pure enough to be of value for other industries, such as the paper industry. The solid residues remaining after extraction can also be environmentally hazardous, requiring additional treatment. Coal fly ash is a combustion residue produced in coal power plants. It is already in a powdery form and so requires no comminution prior to use. However, the Ca content of coal fly ash generated in Korea is low (<10%) since coal power plants mostly use bituminous coals. Accordingly, the carbonation potential is not very high. The amount of waste concrete generated in Korea was about 180,000 tons per day in 2012. Due to the mandatory recycling law, there are about 300 construction waste processing plants in Korea. These plants have typical facilities, such as sorting and crushing units to produce mainly recycled aggregates. For each ton of waste concrete, 180 kg of powdery waste cement is produced (Kim, 2010). This material contains over 40 wt% Ca (as CaO) and is therefore well suited as a raw material for MC due to the availability of fine-grained Ca bearing materials.

The objective of this study is threefold. The first objective is to experimentally analyze MC of waste cement and steel slag. Basic extraction

experiments for each waste type are conducted using hydrochloric, acetic, oxalic, citric acids, EDTA, and ammonium chloride as extraction agents. A review of the literature shows that hydrochloric and acetic acids are commonly used to extract calcium from minerals. It has been reported that the addition of organic acids (oxalic and citric acids) and ligands (EDTA) improves olivine dissolution rates around the near-neutral pH area. Ammonium chloride is known to be the most promising option of these, given the potential it affords for reagent recovery and reuse. However, there has been no actual test to determine whether it can be reused. The second objective is to evaluate the recyclability of the NH_4Cl solution, with additional tests conducted in a cyclical manner. The potential for direct carbonation with flue gas is also evaluated to determine more effective forms of CO_2 sequestration without carbon capture.

The final objective is to perform a thermodynamic simulation of MC using PHREEQC, which is a thermodynamic modeling program that simulates various chemical reactions and transport processes in diverse environments, including in natural or polluted waters. In particular, the program is very useful to model the composition and behavior of dissolved ions and minerals in water. PHREEQC is therefore used in this study to

improve understanding of acid extraction of waste cement and of calcium carbonate precipitation.

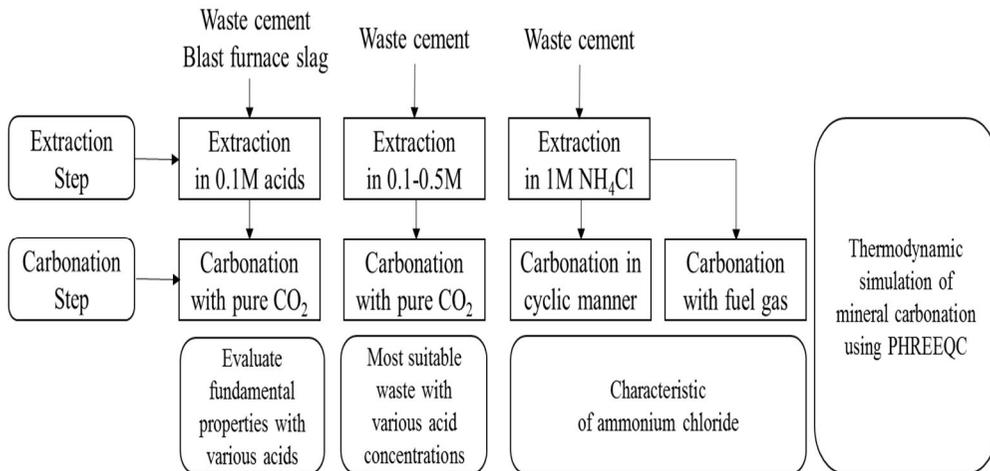


Figure 1-3. Flow chart of the study.

Chapter 2 Literature review

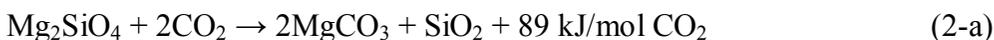
2.1. Selection of suitable materials

In order to provide for sufficient storage of CO₂ through MC, large amounts of raw materials are required as feedstock. Selected raw materials should therefore be easy to obtain and abundant. Both oxides and hydroxides of alkali and alkaline earth metals represent perfect materials for MC, but alkali carbonates are soluble in water and release CO₂ back into the atmosphere. Furthermore, a number of other metals (Mn, Fe, Co) that could possibly be reacted with CO₂ are too rare to be practical for use in sequestration (Brownlow, 1996). Magnesium and calcium are commonly found in mineral silicates. The Earth's crust consists of roughly 2 mol-% magnesium and 2 mol-% calcium, primarily as carbonates and silicate minerals (Goff et al., 1998). Silicate rock therefore appears to offer suitable metal oxide-bearing minerals.

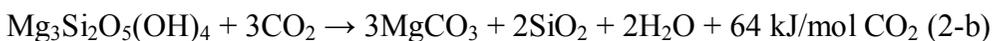
2.1.1. Mineral resources

Among the most suitable sources of natural silicate mineral are olivine (Mg_2SiO_4 ; Equation 2-a), serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$; Equation 2-b), and wollastonite (CaSiO_3 ; Equation 2-c), all of which have relatively high calcium or magnesium content.

Olivine:



Serpentine:



Wollastonite:



In addition, there are other minerals that have been used for carbonation, including feldspar ($\text{CaAl}_2\text{Si}_2\text{O}_8$), forsterite (Mg_2SiO_4), pyroxene ($\text{CaMgSi}_2\text{O}_6$) and talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$). These minerals were used extensively in earlier studies on MC (Huijgen et al., 2006, Fauth et al., 2000). Although they are abundant, as research on MC continues to grow, the amount of suitable mineral deposits becomes a more important consideration. The total estimated volume of CO_2 fixation, is calculated based on domestic reserves, with CO_2 fixation rates given in Table 2-1. Reserves are estimated to total

about 13 Mt, approximately 2.5% of total annual CO₂ emissions in Korea (600 Mt).

The natural silicate olivine could be used efficiently (about 57% alkaline content) but is not suitable for carbonation in the absence of mines for this mineral in Korea. Domestic reserves of serpentine are the largest (among candidate minerals), and it thus the most suitable option for carbonation in the country. However, when considering the potential amount of CO₂ fixation and the size of natural mineral reserves, there are no significant practical benefits to be derived from using natural minerals. Moreover, when industrial scale mineral-based sequestration is considered, mineral resources will become a limiting factor. Utilization of these minerals also requires large-scale mining operations that often face criticism regarding cost and environmental issues arising from exploitation of natural resources.

Table 2-1. Production capacity and CO₂ fixation potential for utilizing domestic natural minerals. (Research report of KIGAM, 2008)

Natural minerals	Alkali content [%]	Estimated Reserve [Mt]	CO ₂ fixation potential	
			Rate [%]	Amount [Mt]
Wollastonite	43.3	5.4	34.0	1.8
Serpentine	43.7	18.0	48.1	8.66
Talc	31.9	7.7	35.1	2.70
Olivine	57.3	–	63.0	–
Total		31.1		13.2

2.1.2. Industrial wastes

Recently, there has been increasing interest in MC using alkaline industrial wastes, such as steel-making slag, waste concrete, asbestos-mining tailings, and coal fly ash (Eloneva et al., 2008, Teramura et al., 2000, Wilson et al, 2009, Montes-Hernandez et al., 2009). Other materials that have been utilized in either laboratory or pilot-scale evaluations of carbonation technology are given in Table 2-2. In general, the selected materials are residues of high temperature combustion processes or derived from construction. Industrial wastes that are alkaline, inorganic, and rich in Ca and Mg, can be applied as an alternative feedstock for mineral CO₂ sequestration.

Wastes have a number of advantages compared to minerals. They are available near industrial areas, they cost little, and they have higher reactivity due to their chemical instability (open structure). An example is provided by comparing the rate of calcium extraction from waste cement using an acetic acid solution (Figure 2-1), with results for wollastonite under the same conditions. The extraction rate of calcium from waste cement is much higher than that from wollastonite. The unstable nature and potentially higher reactivity of many calcium-containing industrial residues could be useful for purposes of CO₂ sequestration. Another beneficial effect of this approach is that harmful heavy metals can be fixed during carbonation (Bertos et al., 2005).

Table 2-2. Wastes that have been utilized for carbonation and their usual disposal routes. (Bertos et al., 2004)

Waste	Description	Usual Disposal Routes
Galligu	By-product of the manufacture of sodium carbonate	Dumped in pits and covered with ash.
MSWI ash	Ash from combustion of municipal solid wastes	Incorporated into materials for construction applications.
Cyclone dust	Air pollution control waste	Landfilled.
Cupola furnace dust	Waste dust originating from metal casting furnaces	Landfilled.
Sewage sludge	Waste product from wastewater treatment	Stabilization with cement
Cement kiln dust	Partially calcined mineral mixture	Agricultural applications
Air pollution control residues	Combined material collected in electrostatic precipitators	Used for cement production.

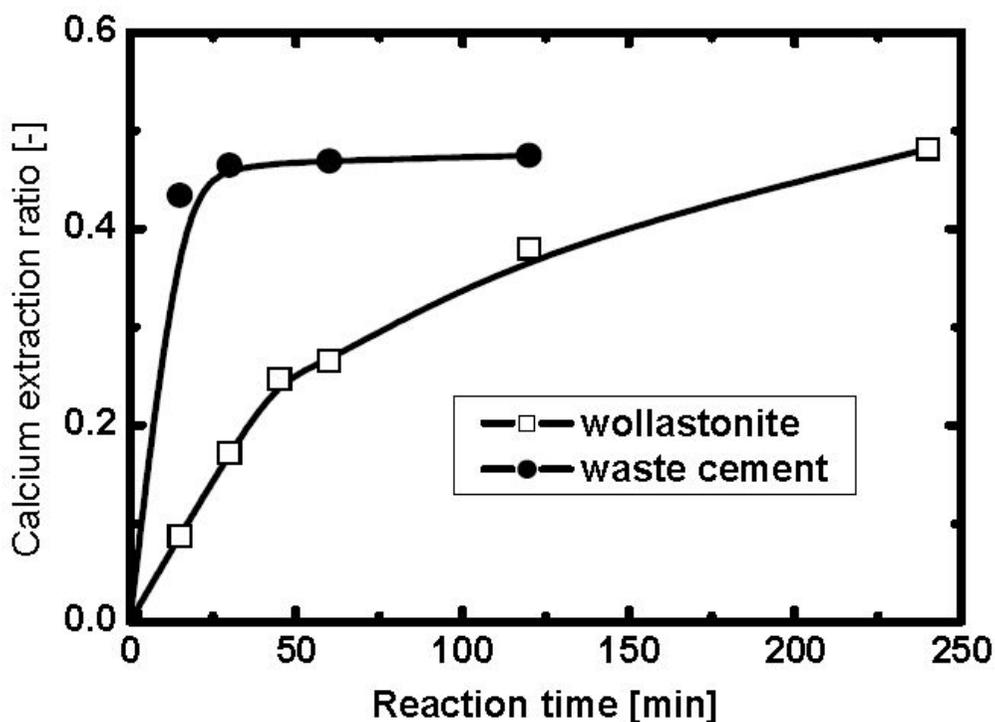


Figure 2-1. Calcium extraction rates for wollastonite and waste cement powder using acetic acid solution (25.76 %) at 333 K. (Yamasaki et al., 2006)

Table 2-3 summarizes annual generation of various industrial wastes available for use in MC, their alkali metal-containing properties for carbonation, and the estimated amount of CO₂ fixation they would provide. While approximately 13 Mt of minerals are available for MC (Table 2-2), more than 50 Mt of domestic industrial wastes are generated annually, and the available amount of CO₂ fixation using the latter could exceed about 12

Mt. It is furthermore possible to ensure a stable supply, with continuous generation every year.

Table 2-3. Production capacity and CO₂ fixation potential utilizing domestic industrial by-products. (Korea Institute of Geoscience and Mineral Resources, 2008)

Industrial wastes	Production [Mt/yr]	Alkali metal content [%]		Metal oxide amount [Mt/yr]			Potential amount of carbonates [Mt/yr]			
		Ca	Mg	Ca	Mg	Sum	CaCO ₃	MgCO ₃	Residue	
BF	10.2	40.0	8.6	3.2	0.97	4.2	7.3	1.8	5.3	
Slag	Convert	9.0	41.5	6.5	2.9	0.64	3.6	6.7	1.2	4.7
	Fe- Ni	1.0	0.3	31.3	0	0.34	0.35	0	0.66	0.68
Waste concrete	30.0	15.0	1.4	3.5	0.46	4.0	8.0	0.88	25.0	
	Coal	5.8	7.5	1.7	0.34	0.11	0.45	0.78	0.21	5.3
Ash	MSWI	0.4	5.4	2.6	0.01	0.01	0.02	0.03	0.02	0.37
	Asbestos	0.09	0	43.3	0.4	0.04	0.04	0	0.08	0.05
Total	56.5	–	–	10.0	2.6	12.6	22.8	4.9	41.4	

2.2. Carbonation process routes

After MC was originally proposed in 1990 (Seifritz, 1990), many studies determined various ways to enhance carbonation reactions. Some of these included pre-treatment of the feedstock. Pre-treatment options are here discussed first, followed by a description of MC routes.

2.2.1. Pre-treatment of feedstock

Activation of MC can be achieved by heat-treatment and by ultrafine grinding before carbonation, as shown in Table 2-4.

In order to increase the reaction rate, materials can be ground to increase their surface area. The influence of particle size on conversion has been investigated (O'Connor et al., 2000); a reduction from 106–150 μm to $< 37 \mu\text{m}$ was found to increase the reaction rate in these experiments from 10% to 90%. However, this process is too expensive and energy-intensive (70–150 kWh/ton).

Thermal activation has been studied to activate serpentine for carbonation (O'Connor et al., 2002). This mineral commonly contains 13 wt% chemically bound water. The hydroxyl groups in serpentine were removed via heat-treatment at 600–650 °C, and an open structure was created. With

grinding, a significant improvement in the carbonation rate was obtained (as above), but the energy required was estimated to be 300 kWh/ton of mineral. As a result, pre-treatments can be considered to be unfeasible from the energy point-of-view, and rendering it impossible for these options to be applied in practice.

Table 2-4. Mineral carbonation CO₂ storage costs. (O'Connor et al., 2005)

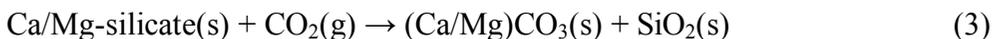
Ore (type of pre- treatment)	Conversion after 1 hour (%)	Cost (US\$/t ore)	Energy input (kWh/tCO₂ stored)	Cost (US\$/tCO₂ stored)
Olivine (standard)	61	19	310	55
Olivine (activated)	81	27	640	59
Antigorite (standard)	62	15	180	250
Antigorite (activated)	92	48	1010	78
Wollastonite (standard)	43	15	190	91
Wollastonite (activated)	82	19	430	64

2.2.2. Direct carbonation

Direct carbonation of a mineral is conducted in two major ways: through a direct dry gas-solid reaction or in an aqueous solution.

Gas-solid carbonation

The direct reaction of gaseous CO₂ with solid mineral or industrial waste is the simplest approach. This reaction scheme is as follows:

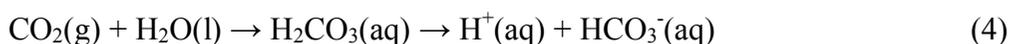


However, the reaction rate is too slow and the process requires high temperature and pressure to increase kinetics. Even under such conditions, the reaction is thermodynamically limited because it is a gas-solid reaction. This method is therefore regarded as unsuitable for industrial application and research has since focused on indirect or multi-step gas-solid carbonation. Two research groups are still studying this process using reactive wastes, but this route is unlikely to develop beyond the research stage (Reddy et al., 2008, Baciocchi et al., 2009).

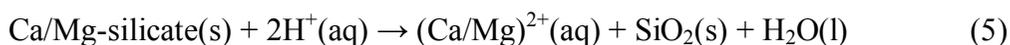
Aqueous carbonation

The presence of water significantly enhances the carbonation reaction rate in natural weathering processes. Direct aqueous MC, performed in a

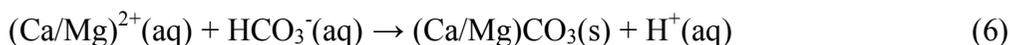
single step in an aqueous solution, appears to be the most promising CO₂ mineralization alternative (Huijgen, 2007). This process involves three mechanisms, which occur simultaneously in a single reactor (O'Connor et al., 2000). First, carbon dioxide dissolves in the water phase resulting in a mildly acidic environment with HCO₃⁻ as the dominant carbonate species:



Second, Ca/Mg leaches from the mineral matrix, facilitated by the protons present:



Finally, magnesium or calcium carbonate precipitates:



In these reactions, silicate dissolution is the rate-limiting step, and as a result, efforts have focused on improving the kinetics of silicate dissolution using various additives and by increasing operating conditions, such as temperature and pressure. Although a high degree of carbonation has been achieved, the process is still too expensive to be applied on a large scale (Huijgen et al., 2005).

A number of researchers have recently investigated this route for conversion of various minerals, such as forsterite and brucite, or alkaline industrial wastes, such as air pollution control (APC) residue, stainless steel

slag, and bottom ash (Kwak et al., 2010, Zhao et al., 2010, Baciocchi et al., 2008).

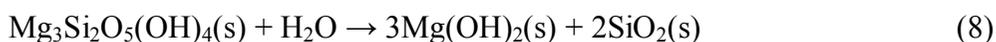
2.2.3. Indirect carbonation

Indirect carbonation is conducted in two steps to achieve a higher degree of carbonation: extraction of the reactive component (Mg or Ca) from the minerals, followed by carbonation during which the extracted components are reacted with CO₂. The process can be also divided into gas and liquid phases, depending on the reaction conditions.

Multi-step gas-solid carbonation

Slow reaction kinetics could be overcome by dividing gas-solid carbonation into several steps. This method of carbonation (Ca/Mg)O proceeds much faster than gas-solid carbonation using Ca/Mg silicates. The process involves extraction of metal oxide under atmospheric conditions, followed by elevated temperature (500 °C) and pressure (20 bar) to achieve reasonable carbonation reaction kinetics (Zevenhoven et al., 2008). For serpentine, this implies the following chemical formulae:





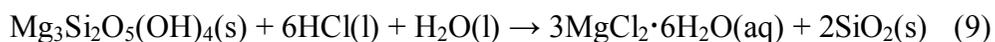
The production of magnesium hydroxide is currently being investigated for improvement of energy economics, due to the unfavorable thermodynamics of the reaction and hydration of MgO to Mg(OH)₂. Mg(OH)₂ under atmospheric conditions may also be carbonated at elevated temperature and pressure to render the chemical kinetics faster. This route also appears to show faster combination kinetics, especially for larger particles (Zevenhoven et al., 2008). However, there is insufficient evidence of its industrial viability for use at high temperatures and pressures.

Aqueous carbonation

Indirect aqueous carbonation refers to processes that take place in more than one stage and involve water. This method of carbonation typically involves the extraction of reactive components from minerals, using strong acids or other solvents, followed by the reaction of the extracted components with CO₂ in order to speed up aqueous carbonation. The advantage of this route is that the two steps can be optimized separately. During the extraction step, excess acid is required to achieve high extraction efficiency, and in turn, the pH of the extraction solution can be very low. This inhibits the subsequent carbonation reaction, which favors basic pH conditions. It is

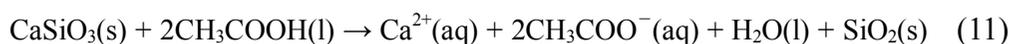
therefore necessary to increase the pH prior to carbonation. If a caustic reagent is used for this purpose, a considerable quantity of reagents would be required for the extraction and carbonation steps. One remaining challenge is that, in all cases, acid recovery is difficult. However, this approach improves the feasibility of producing valuable pure materials for further application.

HCl extraction route. Hydrochloric acid (HCl) dissolution of serpentine or olivine was first proposed by Barnes et al. (1950). The process requires a number of steps to precipitate magnesium hydroxide, which can then directly react with gaseous CO₂. HCl is then recovered by boiling off the aqueous phase:



Major weaknesses of this route are the costs associated with the use of HCl, which requires recovery and corrosion resistant facilities, and the energy consumption caused by the evaporation step. It was shown that most of the energy is consumed during dehydration and crystallization steps. Total sequestration costs were estimated at over 233 US\$/t CO₂ (Newall et al., 2000).

Acetic acid extraction route. The use of acetic acid offers one approach to reduce the consumption of energy and acid, as shown in Figure 2-2 (Kakizawa et al., 2001, Teir et al., 2007). This method consists of two steps. The first step is the extraction of calcium ions from calcium silicate with acetic acid:



The solid SiO_2 precipitates and is separated using a thickener. When gaseous CO_2 is injected into the solution, calcium carbonate is crystallized and the acetic acid is recovered in a combined step:

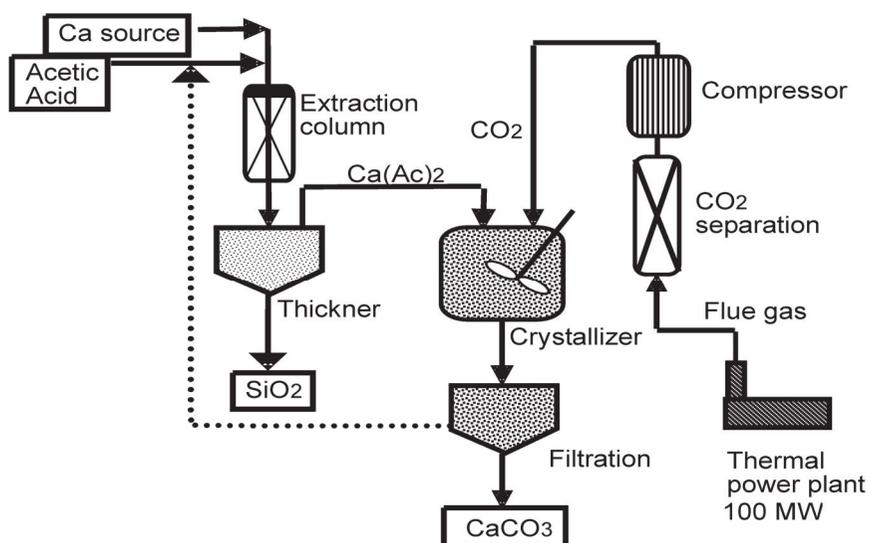


Figure 2-2. Schematic drawing for the CO_2 disposal process. (Kakizawa et al., 2001)

At 1 bar, 40% of theoretical conversion can be achieved; 75% can be achieved at 30 bar. The main advantage of this route is the ability to speed up the carbonation process with a less severe extraction medium and the ability to recover acetic acid during the second step. The total costs (including separation, compression, and pulverization costs) of this method were estimated at 55 US\$/t CO₂.

Chemically-enhanced aqueous carbonation. The promotion of MC has been investigated using various chemicals. If the rate-limiting step in the aqueous carbonation is action of carbonic acid reacting with magnesium or calcium, then the production of carbonates may be achieved via a dissolution stage.

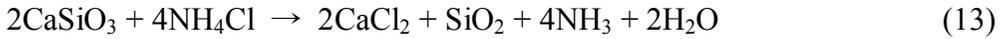
As the quantity of reactive magnesium is the limiting reagent, various solvents have been used to enhance the dissolution of magnesium (Park et al., 2003). Complex agents have been used to polarize and weaken magnesium bonds within the serpentine structure and to increase Mg solubility. Among the various agents studied, orthophosphoric acid, oxalic acid, and ethylenediamine-tetraacetic acid (EDTA) achieved magnesium ion concentrations 1.5 times higher than those of hydrochloric acid under mildly acidic conditions. This is because the former can keep either silicates or magnesium ions in solution by forming water-soluble complexes. In large scale industrial

application, any use of chemicals without recycling should be avoided for both cost and environmental reasons. Any additive used to enhance the carbonation process should therefore be carefully selected. Unfavorable, irreversible reactions caused by the addition of multiple chemicals can also make the process unfeasible.

Organic acid. Organic acids have also been investigated for MC, in order to reduce the energy penalty associated with strong acids. It has been reported that the sodium salt of organic acids such as citric acid is effective and has strong chelating properties (Carey et al., 2003). In this process, fine serpentine was reacted in a solution with dissolved salts under a CO₂ atmosphere, at 120 °C. This energy consumption could be avoided by dissolving the serpentine in an essentially weak acid. This would also reduce the amount of caustic reagent needed in the second step. For these reasons, development of this process has steadily progressed recently, even though the main problem (acid recycling) remains largely unsolved.

Extraction using recyclable ammonium salts. There have been several other attempts to develop a process with full chemical recycling to improve the efficiency of MC. Kodama et al. developed a process that uses NH₄Cl as an

extracting agent (see Figure 2-3). It was reported that NH_4Cl could dissolve calcium ions efficiently and selectively from slag:



After removing the slag residue, injection of CO_2 into the leaching solution resulted in the precipitation of pure calcium carbonate and NH_4Cl was regenerated during carbonation:



A caustic reagent was not required for carbonation in this process as the solution pH was stabilized in the alkaline region during extraction.

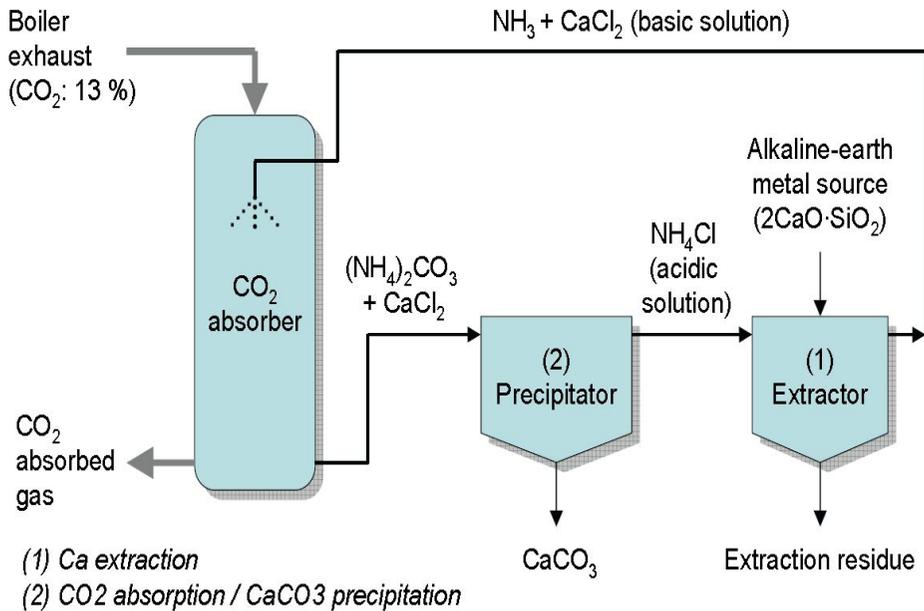
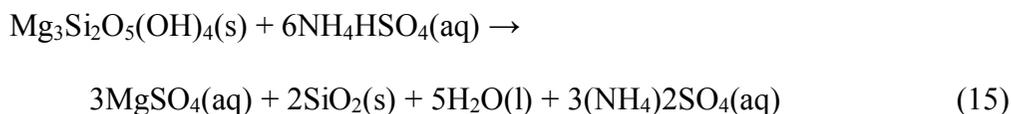


Figure 2-3. Flow diagram of a full chemical recycling process. (Kodama et al., 2008)

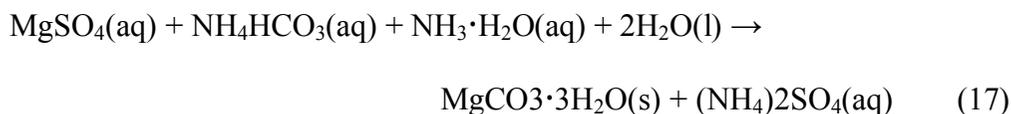
Maroto-Valer et al. (2011) also developed a pH-swing CO₂ mineralization process to analyze the use of various ammonium salts. In this process, aqueous NH₄HSO₄ was used to extract Mg from serpentine. At 100 °C, 1.4 M NH₄HSO₄ was found to extract 100% of Mg in three hours. The pH of the solution was then controlled using aqueous ammonia, resulting in iron and silicon precipitating from solution. Subsequently, NH₄HCO₃ and NH₃ were added to the solution to react with Mg and produce carbonates. After this (NH₄)₂SO₄ was recovered from solution by evaporation. This chemical reaction is represented in the following equation:



After dissolution, the pH of the solution was increased to alkaline values. The chemical reaction of pH regulation is shown as follows:



The reaction of precipitation by treating MgSO₄ with NH₄CO₃ and NH₃ is presented in the following equation:



The formation of magnesium carbonate species depends on temperature and pressure (Hanchen et al. 2008). The final step is additive

regeneration, with decomposition of $(\text{NH}_4)_2\text{SO}_4$ at 330 °C, and production of NH_3 for the capture step and NH_4HSO_4 for the dissolution step.

These processes seem to be promising given the potential for reagent recovery and reuse. The main drawback of the aqueous pH swing ammonium based process is the large amount of water and energy needed separation from salts during the regeneration step. In addition, although the possibility of reuse is mentioned, there are no actual test results.

2.3. Carbonation process for industrial wastes

The process routes used for carbonation of natural minerals can in principle also be applied to the carbonation of industrial wastes. The latter has a number of advantages: (1) these materials are often associated with CO_2 point source emissions; (2) they tend to be chemically less stable than minerals and require a lower degree of pre-treatment; (3) waste materials could supply a readily available source of calcium or magnesium; and (4) the by-product of the carbonation step may be reused in products such as road base or other construction materials. Table 2-5 gives an overview of selected studies on the carbonation of industrial wastes.

Table 2-5. Selected studies on carbonation of residues including process conditions. (Huijgen et al., 2006)

Residue	Carbonation process	T [°C]	pCO ₂ [bar]	d [mm]
Blast furnace slag		25	3	–
Cement-immobilized slag	Supercritical CO ₂	50	250	
Coal fly ash	Aqueous	185	115	–
Coal fly ash	20% moisture	25	2.8	<0.25
Deinking ash		25	3	–
FBC coal ash	Aqueous	155	75	–
FGD coal ash	Aqueous	185	115	–
MSWI ash		25	3	–
MSWI bottom ash	Moisture	20	60 (l)	<10
		40	150 (sc)	
		50	250 (sc)	
OPC cement		25	3	–
Portland cement pastes	W/C: 0.6	59	97	–
Pulverized fuel ash	W/S: 0.1-0.2	25	3	–
Spent oil shale	20% moisture	25	2.8	<0.25
Stainless steel slag		25	3	–
Waste Dravo-Lime	Aqueous	185	115	–

2.4. Comparison of different mineral carbonation routes

Each of the various MC routes identified previously has its own advantages and disadvantages. Direct gas–solid carbonation seems to be an ineffective method for natural magnesium silicates. However, it might be suitable for certain waste materials, which could also benefit from its potential to reduce the dangerous nature of some materials. Stepwise gas–solid carbonation via $\text{Mg}(\text{OH})_2$ seems interesting as it should be suitable for natural magnesium silicates, produces high-temperature heat, and might not consume significant amounts of chemicals. However, $\text{Mg}(\text{OH})_2$ production requires significantly more heat than is generated during carbonation (Zevenhoven et al.,2010).

The direct aqueous carbonation route, and the promising results achieved using it, indicate that it is worthy of further study. Even so, as long as the raw material is carbonated in one step, it is impossible to produce a pure carbonate product. In addition, it seems that certain process conditions are suitable only for specific materials. There might be a need to identify a specific process or at least optimal conditions, for each waste material.

Indirect carbonation based on acids as solvents extracts the reactive element efficiently from the mineral, but only under conditions that are unfavorable for carbonation. The addition of a base therefore neutralizes the

acidity but makes recovery and recycling of chemicals impossible or expensive. This method, based on the use of caustic alkali-metal hydroxide, also suffers from excessive chemical consumption. It was already known that pure calcium carbonate could be produced efficiently from industrial wastes using a weak-base strong acid salt solution and pressure change. However, the recovery of evaporated NH_3 might hinder the economic viability of the former route. The latter was not reported to consume any chemicals, but requires pure carbon dioxide provided by an expensive CO_2 capture process. This problem is also present with direct carbonation processes that require high pressure. As a result, many MC options have been studied, but none has yet been shown to be clearly superior to others.

2.5. Utilization of carbonate products

The effective development of utilization routes for materials produced by MC could help to render this method economically viable and to facilitate its deployment. Based on the information discussed in previous sections, processes where cations are extracted from material in a separate step (indirect processes) may be more suitable for controlling the morphology and

particle size of precipitated products for high-value applications, as compared to direct carbonation (Teir et al., 2005).

Calcium carbonate is used extensively as a functional material in several fields (e.g., plastics, rubber, paint, printing ink, weaving, toothpaste, make-up, and foodstuffs). Calcium carbonate is also needed for indirect processes that use alkaline wastes or calcium silicates, such as wollastonite. Calcium carbonate can precipitate in six different forms (amorphous calcium carbonate (ACC), hexahydrate calcium carbonate (HCC), monohydrate calcium carbonate (MCC), and the polymorphs calcite, aragonite and vaterite) with trigonal, orthorhombic, and hexagonal crystal systems, respectively (Lindeboom et al., 2013). For precipitated calcium carbonate (PCC) applications, several physical and chemical properties are very important in determining the potential market (Tai et al., 1998).

Making PCC from wastes can contribute to the reduction of those wastes that contain high calcium content, such as steel slag. This metal waste can be utilized as PCC, if calcium is selectively extracted prior to carbonation (necessary to fulfill the requirements of purity and crystal shape). Calcium selectively extracted from slag with an aqueous solution of ammonium salt (NH_4NO_3 , $\text{CH}_3\text{COONH}_4$ or NH_4Cl) could produce PCC with properties comparable to PCC produced by conventional methods. However,

a very small liquid ratio (5 g/L) is required to obtain high dissolution efficiency (73%), rendering this method expensive because of the large reactor volumes required (Said et al., 2012). Moreover, calcium carbonate powder produced from steel slag exhibited inferior brightness compared to traditional PCC, which resulted in decreased market value of the alternative product.

Chapter 3 Materials and methods

3.1. Appropriate industrial wastes

A number of potentially suitable industrial wastes are generated in large quantities in Korea, with these including coal fly ash, steelmaking slag and waste concrete, as discussed in Chapter 2.1.

Coal has been used as a major fuel in thermal power plants due to the stability of its supply, its abundance, and its low price. A large number of coal-fired power plants have been built to meet the increasing power demand in Korea. About 28% of total power generated in 2013 was obtained from coal power plants, which produced coal fly ash as a combustion residue (KEPCO in Brief, 2014). Accordingly, the amount of coal ash generated is steadily increasing, and expected to continue increasing in future. It is already in a powdery form and so requires no comminution prior to use. However, the Ca content of coal fly ash generated in Korea is low (<10%) since bituminous coals are most commonly used in coal power plants. Accordingly, the carbonation potential of this kind of coal fly ash is low.

Blast furnace slag is a residue typical of the steel industry. Annual slag generation amounts to 13.9 Mt in Korea (2012), and this amount is expected

to reach 15.6 Mt in 2014 due to the expansion of blast furnace facilities (Kim et al., 2013). The chemical composition of slag varies considerably depending on the composition of the raw materials in the iron production process. The main components of blast furnace slag are CaO (42%), SiO₂ (34%), Al₂O₃ (12%), and MgO (4.8%). In general, increasing the CaO content of slag results in increased slag basicity and an increase in compressive strength. Since the calcium content of slag is greater than 40 wt%, this material has great potential for CO₂ sequestration.

The amount of construction waste generated in Korea was about 180,000 tons per day in 2012 (see Table 3-1). Waste concrete made up 60% of the total (120,000 tons). Due to its mandatory recycling law, Korea has approximately 300 plants for processing construction waste. These plants typically have sorting and crushing units able to produce mainly recycled aggregates. In such facilities, 180 kg of powdery waste cement is produced for every ton of waste concrete, as shown in Table 3-2. As a result, these us 21,600 tons per day of waste cement. This material contains more than 40 wt% Ca (as CaO). It is therefore also suitable for MC and, in addition, contains fine-grained Ca-bearing materials.

Table 3-1. Amount of construction waste generated in Korea. (Report of Korea Waste Association, 2013)

Classification		Amount of waste (ton)
Total construction waste		186,628
Construction and demolition waste	Concrete	117,753
	Asphalt concrete	35,737
	Others	8,051
Combustible materials	Timber	682.7
	Synthetic resins	1,261
	Others	162.7
Inflammable materials	Construction sludge	643.9
	Others	29.4

Table 3-2. Material mass produced from waste concrete. (Kim, 2010)

Total Waste Concrete	Returned Large Block	Recycled Coarse Aggregate	Recycled Fine Aggregate	Residual Cement Material	CaCO₃
1,000kg	350kg	250kg	220kg	80kg	100kg

3.2. Material Processing

Blast furnace slag (size class 250–350 mm) and waste cement (<0.75 mm) were dried in an oven. The slag was crushed by a jaw crusher and ground using a stainless steel mill charged with 200 g of sample and 2 kg of stainless steel balls, as shown in Figure 3-1. The cement could be used without grinding, because it constituted a fine residue recovered from aggregates obtained by crushing demolition concrete waste following size separation.

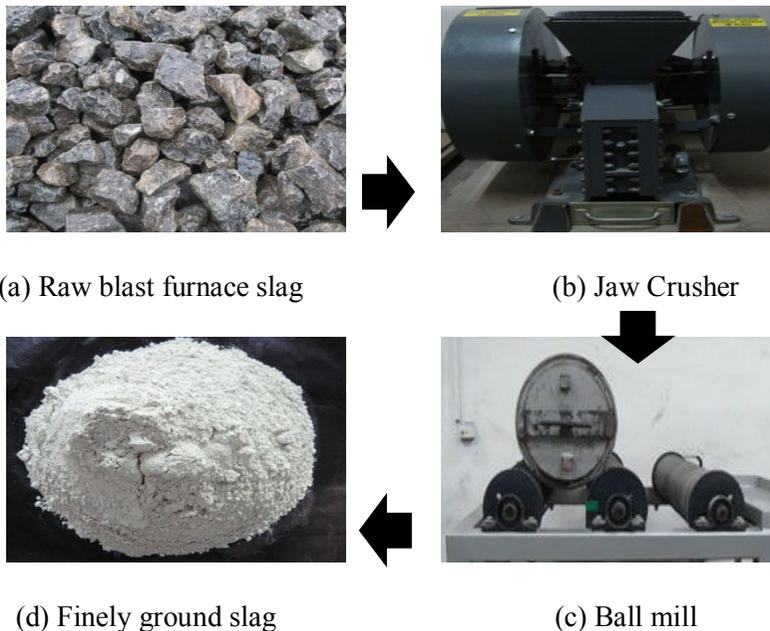


Figure 3-1. Fine grinding process of blast furnace slag in this study.

3.3. Extraction characteristics

To investigate the possibility and potential of producing relatively pure calcium carbonates from alkaline industrial wastes for long-term storage of CO₂, indirect carbonation experiments were conducted. Figure 3-2 shows the overall procedure of these extraction and carbonation experiments.

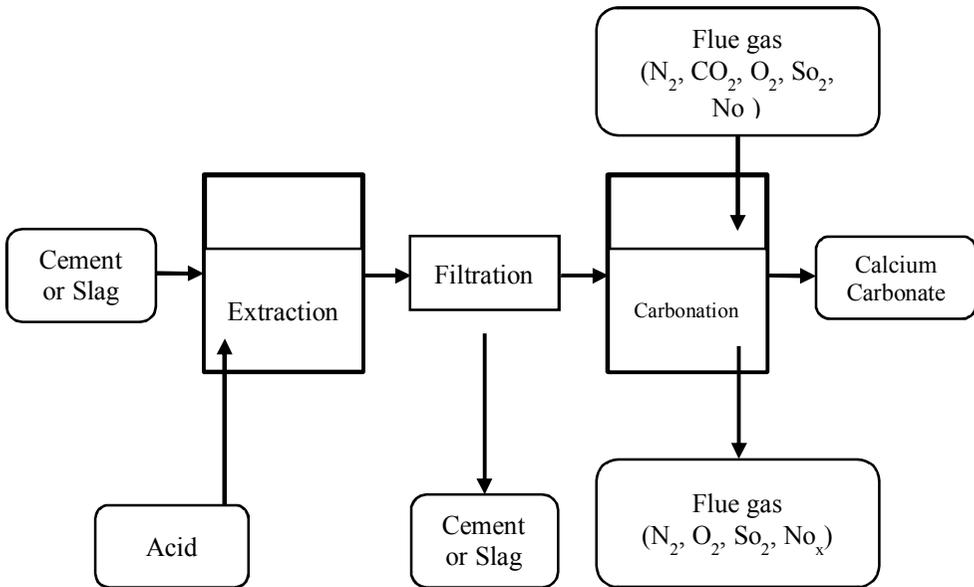
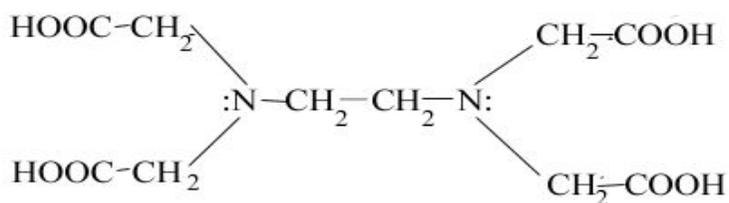


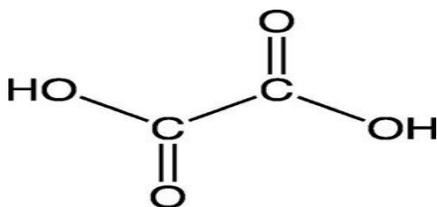
Figure 3-2. Overview of the entire process.

Acetic acid (1 M, Sigma-Aldrich), hydrochloric acid (1 M, Sigma-Aldrich), oxalic acid (0.1 M, Fluka), citric acid (99.5–100.5%, Sigma-Aldrich), EDTA (99%, Sigma-Aldrich), and ammonium chloride (99.5%, Sigma-Aldrich) were used as extraction agents to dissolve the alkaline

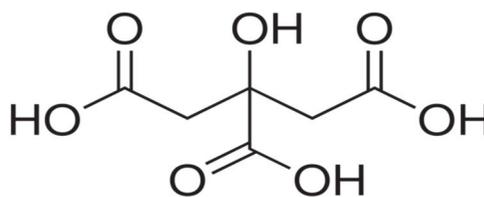
wastes. Figure 3-3 shows the structure of the organic acids and chelating agent.



(a) EDTA



(b) Oxalic acid



(c) Citric acid

Figure 3-3. Structure of chelating compound and organic acids.

Calcium extraction experiments were carried out as follows: 50 g of sample were mixed with 500 mL of acid solution at constant concentration (0.1 M acid) in a 1 L beaker. The slurry was stirred with a magnetic stirrer at 400 rpm, for up to one hour under ambient conditions (25 °C, 1 atm). Liquid samples were obtained at regular time intervals. The concentration of various ions was then analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) in NCEM (ICP-730 ES, Varian).

The ICP is a type of plasma source in which energy is supplied by electric currents produced by electromagnetic induction, that is, by time-varying magnetic fields. ICP discharges relatively high electron density, in the order of 10^{15} cm^{-3} . As a result, ICP discharges have widespread applications wherever high-density plasma is needed.

In order to evaluate the suitability of the sample at various acid concentrations (0.1–0.5 M), additional experiments were conducted using the same process, only varying the acid concentration.

3.4. Aqueous carbonation studies

After one hour of extraction, the slurry was immediately filtered through 6 μm filter paper to separate the solid residue. The filtrate was then poured into a 500 mL flask for carbonation experiments under ambient conditions (25 °C, 1 atm). For the filtrates from HCl and CH₃COOH leachate, the solution pH was adjusted to, and maintained at, pH 10–12 by adding drops of 1 M NaOH solution. After the pH was stabilized, high purity CO₂ gas (99.9%) was introduced at a constant flow rate (100 mL/min) into the flask for two hours to supply sufficient carbon dioxide (open system). The pH of the solution was continuously measured to monitor the progress of the

carbonation reaction. After completion of carbonation, the slurry was filtered and the filtrate was analyzed for Ca and other ions using ICP-OES. The precipitate was collected, washed, and dried before being analyzed using XRD and FE-SEM.

In case of acetic and hydrochloric acids, it was expected that the dissolution of Ca ions would increase with higher acidity. However, the carbonation reaction favors basic pH conditions, so the addition of basic reagents is required to raise the solution to at least pH 8–9 during the carbonation step. Organic acids, which enhance the dissolution of silicates under mild acid conditions, would reduce the agents in the second step. In the case of ammonium chloride, the solution pH becomes alkaline during the extraction step due to the generation of NH_3 . This enhances the absorption of CO_2 into the solution and the precipitation of CaCO_3 without the addition of basic reagents in the carbonation step. Furthermore, the acidic extraction solution and NH_4Cl are regenerated during precipitation of CaCO_3 .

In order to evaluate the recyclability of the NH_4Cl solution, additional tests were conducted in a cyclical manner. First, complete extraction and precipitation were conducted during the first cycle, using the same procedure described above. Then, a second cycle was performed using the filtrate recovered after completion of carbonation during the first cycle as the

extractant, without adding new reagents. These tests were repeated for several cycles and the intermediate products (precipitated calcium carbonates) were dried, weighed and subjected to chemical analysis.

In addition, carbonation experiments were repeated in the same way, using synthetic gases of various compositions in order to evaluate the possibility of carbonation using the flue gas (mixture of CO_2 - N_2 - SO_2 - NO_x). Table 3-3 shows the composition of the synthetic gases tested in this study along with that of the flue gas emitted from coal power plants in Korea. The syngas fuel was supplied from bottled gases mixed to a composition designed for injection into the flasks for the carbonation reaction.

Table 3-3. Compositions of flue and synthetic gases in this study. (Lee et al., 2010, Emission standards acceptable notice of air pollutants, Classification system of air emission facility, Improvement plan of the permit system or appropriation in Korea, 2012)

Component (Vol%)	Flue gas	Synthetic gas
N ₂	75–80	70–90
CO ₂	10–20	10–30
O ₂	5–9	–
SO ₂	0.02–0.54	0.7–0.9
NO _x	0.02–0.53	0.7–0.9

3.5. Characterization of materials

In order to evaluate the suitability of fine waste cement and blast furnace slag for MC, the characteristics of the samples were analyzed in various ways. All the analysis equipment used in this experiment is shown in Figure 3-4.

Analysis of particle size is an important factor in the carbonation reaction, and sieve size analysis was used to determine the median diameter of waste particles.

The Brunauer–Emmett–Teller (BET) gas adsorption method can explain the physical adsorption of gas molecules on a solid surface and serves as the basis for the measurement of the specific surface area of a material. The concept of the theory is an extension of the Langmuir theory, which deals with monolayer molecular adsorption, to include multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb onto a solid in an infinite number of layers; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is as follows:

$$\frac{1}{v \left[\left(\frac{p_0}{p} \right) - 1 \right]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0} \right) + \frac{1}{v_m c} \quad (18)$$

where p and p_0 are the equilibrium and the saturation pressure of adsorbents at the temperature of adsorption, v is the adsorbed gas quantity (in volume units), v_m is the monolayer adsorbed gas quantity and c is the BET constant, defined as follows:

$$c = \exp \left(\frac{E_1 - E_L}{RT} \right) \quad (19)$$

where E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction. The BET method is widely used for calculation of surface areas of solids by physical adsorption of gas molecules. In this study, a BET measuring device using

this theory was used in our laboratory for determining the surface area of wastes (GEMINI V, Micromeritics).

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics, and building materials. XRF spectrometry conducted at the National Instrumentation Center for the Environmental Management College of Agriculture and Life Sciences (NICEM, Seoul National University) was used for measuring the chemical composition of wastes (S4 PIONEER, Bruker AXS).

X-ray diffraction is a tool used for identifying the atomic and molecular structure of a crystal; atoms in a crystal cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other aspects. The structure of wastes was measured by Powder X-Ray Diffractometry at NICEM (D5005, Bruker).

A Field Emission-Scanning Electron Microscope (FE-SEM) is able to observe small structures on the surface of materials using electrons (particles with a negative charge) instead of light. Electrons are liberated from a field emission source and mineral in a high gradient electrical field. Within the high vacuum column these so-called primary electrons are focused and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result secondary electrons are emitted from some spot on the object. The angle and velocity of these secondary electrons relates to the surface structure of the object. A detector catches the secondary electrons and produces an electronic signal, which is amplified and transformed to a video scan-image that can be seen on a monitor. In this study, images of the surface structure of the samples were produced by FE-SEM (SUPRA 55VP, Carl Zeiss) at NICEM.



(a) BET gas adsorption



(b) FE-SEM



(c) ICP-OES



(d) WDXRF spectrometry



(e) X-Ray Diffractometry

Figure 3-4. All analysis equipment used in this experiment.

Chapter 4 Experimental results

4.1. Analysis of alkaline wastes

In order to evaluate the suitability of alkaline wastes, the characteristics of the samples were analyzed in various ways. The particle size distribution of waste cement and blast furnace slag is shown in Fig. 4-1, with these having a median diameter of 28.61 μm and 31.59 μm respectively. BET measurement results showed that their respective specific surface areas were 13 m^2/g (waste cement) and 0.71 m^2/g (blast furnace slag).

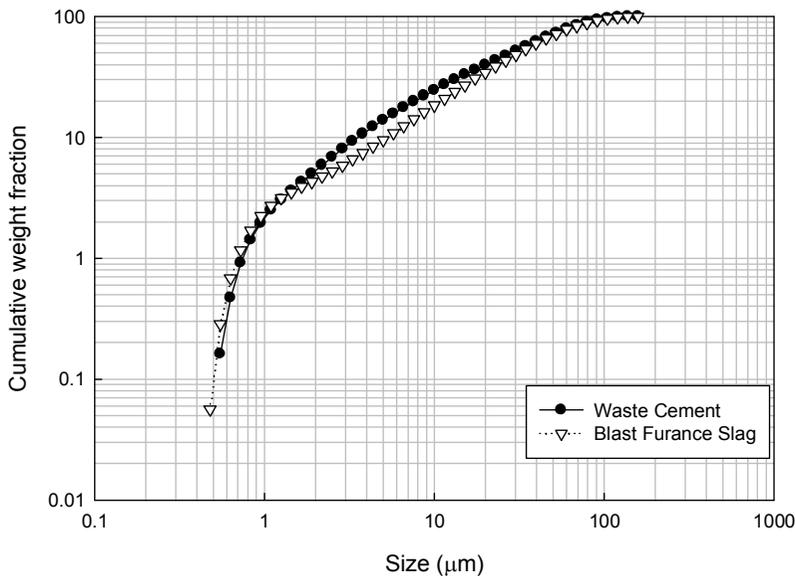


Figure 4-1. Cumulative size distribution of waste cement and blast furnace slag.

The chemical composition of waste cement and slag were determined using XRF. As shown in Table 4-1, the materials had similar composition, being rich in Si, Ca, Al, Fe, K, and Mg, and with the presence of minor elements: Na, Ti, and Mn. These wastes were shown to be highly suitable for mineral CO₂ sequestration because of their high Ca content and high alkalinity. In terms of suitability for carbonation, slag showed more abundant Ca content in comparison with cement.

Table 4-1. Chemical compositions of waste cement and slag.

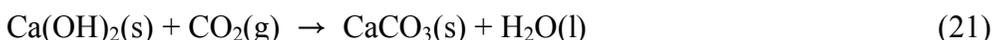
Formula	Waste Cement	Blast Furnace Slag
	wt%	wt%
SiO ₂	39.1	31.84
CaO	37.95	45.84
Al ₂ O ₃	9.83	14.4
Fe ₂ O ₃	4.98	0.68
K ₂ O	2.27	0.51
SO ₃	2.08	1.67
MgO	1.98	3.62
Na ₂ O	0.74	0.25
TiO ₂	0.48	–
MnO	0.16	0.39

The theoretical maximum CO₂ uptake (tCO₂ uptake) of wastes expressed in wt% was calculated using a modified Steinour formula (Sanna et al., 2012).

$$\begin{aligned} \text{tCO}_2 \text{ uptake} = & 0.785 \times (\% \text{CaO} - 0.7 \times \% \text{SO}_3) + 1.091 \times \% \text{MgO} \\ & + 0.71 \times \% \text{Na}_2\text{O} + 0.468 \times (\% \text{K}_2\text{O} - 0.632 \times \% \text{KCl}) \end{aligned} \quad (20)$$

Table 4-2 presents a summary of inorganic waste materials that have been tested as MC feedstocks. This method is based on the assumption that all Ca and Mg in waste can be extracted and subsequently carbonated. Based upon previous XRF analysis data, waste cement and blast furnace slag used in this study were expected to be able to take up 32.39%, and 39.43%, respectively. These are higher values than in those indicated in literature.

XRD analysis (Figure 4-2) revealed that the primary Ca mineral present in waste cement is portlandite ($\Delta H_f = -68$ kJ/mol), which is carbonated relatively easily (Huijgen et al., 2003), according to the following formula:



However, XRD analysis of slag was difficult due to its amorphous structure.

An FE-SEM image of waste cement particles shows a distinct porous structure that may allow rapid penetration of liquid into the solid phase. On the other hand, the vitreous structure of slag was expected to be relatively

impervious to the solution (Fig. 4-3). All of these properties suggested that slag and waste cement were appropriate materials for MC.

Table 4-2. Main properties and carbonation conversions of waste materials. (Sanna et al., 2013)

Material	CaO (%)	MgO (%)	tCO₂ (%)
Blast Furnace Slag	15–42	5–11	20–44
Basic Oxygen Furnace Slag	34–56	2–6	29–52
Electric Arc Furnace Slag	25–47	4–19	24–48
Cement Kiln Dust	34–48	1–1.5	10–30
Cement Bypass Dust	66	1	50
Waste Cement	25–63	0.3–2	20
Municipal Solid Waste Incineration Ash	22–53	2.8	25
Air pollution control	36–60	1–2.5	50–58
Coal Fly Ashes	1.3–10	1–3	6–9
Wood ash	24–46	8–9	50

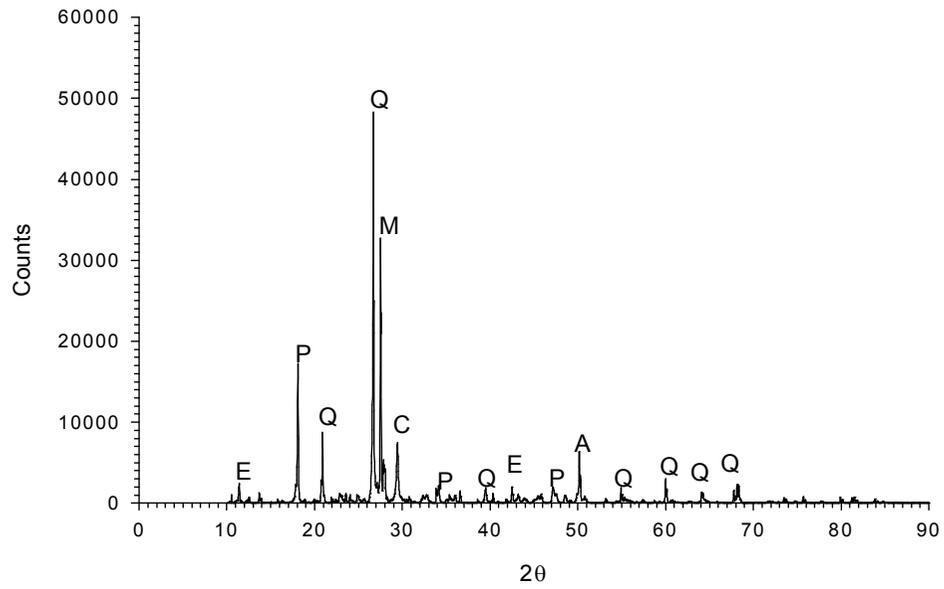
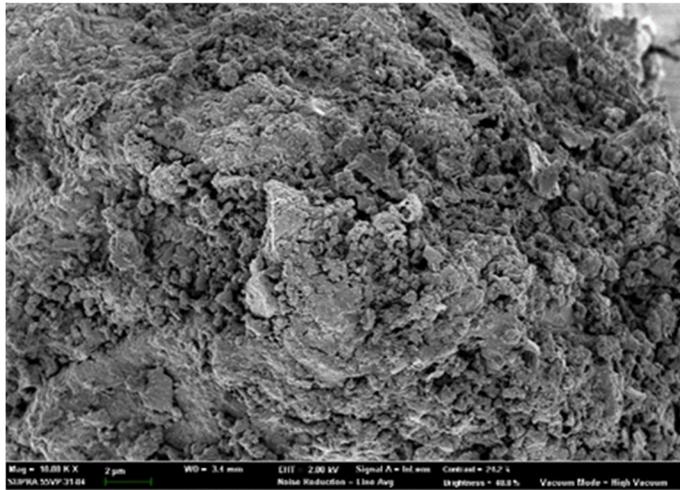
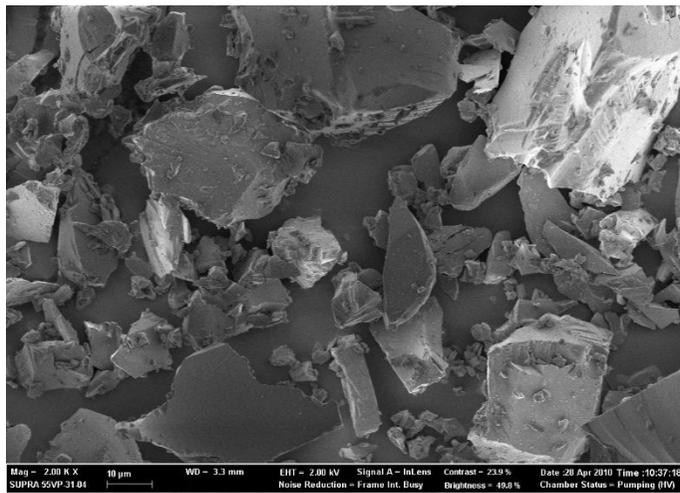


Figure 4-2. XRD peaks obtained on analysis of waste cement (A: albite, C: calcite, E: ettringite, M: microcline, P: portlandite, Q: quartz).



(a) Waste Cement



(b) Blast Furnace Slag

Figure 4-3. Surface morphology, as captured by FE-SEM.

4.2. Extraction characteristics of alkaline wastes

In order to compare the extraction efficiencies of waste cement and blast furnace slag, the reactions were run for up to one hour. Figure 4-4 shows variations in calcium concentration with reaction time using different solutions containing 0.1M acid. In all cases, the initial reaction was rapid and stabilized after several minutes. This was attributed to disordering of the crystal surfaces during grinding. In the waste cement (Figure 4-4a), the maximum calcium concentration extracted by HCl and CH₃COOH was 2,400 mg/L. NH₄Cl showed a slightly lower dissolution ability than HCl and CH₃COOH (2,000 mg/L). Although citric acid (500 mg/L) showed greater dissolution ability than oxalic acid (200 mg/L), it barely extracted calcium ions from waste cement, when compared to other acids. In contrast to previous studies in the literature, citric acid and oxalic acid had little effect on cement dissolution. EDTA is a weak acid, but it was found that the extraction rate for EDTA alone (2,700 mg/L) was higher than that for all other acids. All acids showed a high selectivity for calcium in waste cement ($\geq 99\%$). When EDTA was added to HCl and CH₃COOH (Table 4-3), the calcium concentration (5,000 mg/L) was approximately two times higher than for 0.1 M CH₃COOH. In the case of the HCl solution (4,700 mg/L), the role of EDTA was less significant than that of acetic acid. Although the

addition of EDTA could increase extraction, it was relatively ineffective in milder conditions, as reported in previous studies

When various acids (with the exception of citric and oxalic acids) were added to the slag (Figure 4-4b), the addition of EDTA produced the same effect. However, in the case of slag, the maximum calcium concentration (1,800 mg/L in HCl, 1,500 mg/L in CH₃COOH), selectivity for calcium (80–95%), and equilibrium pH (5–8) were lower than those for waste cement (Table 4-4). In particular, NH₄Cl had very low reactivity with slag. The low calcium concentration was attributed to the low specific surface area of slag compared with that of waste cement. This reduced acid penetration and the availability of surface reaction sites. Slag contains many potentially hazardous heavy metals that could be leached out, resulting in low calcium concentrations during extraction. Heavy metals, such as zinc, lead, copper, and cadmium, which are bound to or associated with sulfides in blast furnace slag, show a relatively high availability for leaching, especially if stable oxidizing conditions are maintained (Tossavainen, 2005). This could complicate the process and the resulting carbonated products may not be of sufficient purity to be of value for other applications, such as in the paper industry. Moreover, post-extraction residues can be environmentally hazardous and may require additional treatment.

Table 4-3. Ion concentrations and equilibrium pH in a variety of 0.1 M acid sets after one hour of reaction (waste cement).

Additives	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Al (mg/L)	Si (mg/L)	Equilibrium pH
HCl	2421	0.08	0	0.88	2.07	12.27
CH ₃ COOH	2444	0.09	0	1.11	3.09	12.11
NH ₄ Cl	2095	0.66	0	0.83	4.51	11.32
EDTA	2744	0.87	0	1.46	3.80	11.24
HCl + EDTA	4771	6.44	0	0.01	15.02	10.02
CH ₃ COOH + EDTA	4931	4.77	0	0.01	23	10.1

Table 4-4. Ion concentrations and equilibrium pH in a variety of 0.1 M acid sets after one hour of reaction (blast furnace slag).

Additives	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Al (mg/L)	Si (mg/L)	Equilibrium pH
HCl	1816	129.9	5.8	0.52	103.9	6.98
CH ₃ COOH	1502	111	39.86	5.37	95.31	5.66
NH ₄ Cl	151.63	5.40	0	0.01	2.49	8.37
EDTA	1949	133.1	147.4	143.9	92.72	6.26
HCl + EDTA	3370	235.7	138.5	280.7	89.46	5.95
CH ₃ COOH + EDTA	4017	20.16	240.6	420.6	120.6	5.35

4.3. Production of calcium carbonate from industrial wastes

After one hour of extraction, calcium-rich solutions from each waste product were reacted with 99.9% CO₂ to precipitate calcium carbonate. The extraction solutions of 0.1 M CH₃COOH and 0.1wt% EDTA were selected as the most effective for both blast furnace slag and waste cement. Even though these solutions had high calcium concentration (4,900 mg/L from cement and 4,000 mg/L from slag), indicating 32% and 22% of theoretical maximum CO₂ uptake, respectively, they did not produce CaCO₃ by injection of CO₂ because the solution pH rapidly dropped to acidic conditions. It was therefore necessary to adjust pH by adding NaOH in order to induce effective carbonation. As pH was increased with the addition of NaOH, calcium ions in solution were converted into calcium carbonate, as shown in Figure 4-5. The extent of carbonation calculated from reductions in the calcium concentration were 18% at pH 10 and 31% at pH 12 in the case of cement. Slag showed a lower degree of carbonation than cement.

Figures 4-6 and 4-7 shows solid products analyzed by SEM-EDS and XRD. The solid product obtained from waste cement occurred as white particles of uniform size (under 3 μm) and was very pure calcite. Although the product from slag was verified by XRD data, it had light brown and heterogeneous particles that lowered its quality, mainly due to the presence

of silicate and aluminate. Waste cement was therefore considered a more appropriate material for the production of relatively pure calcium carbonate.

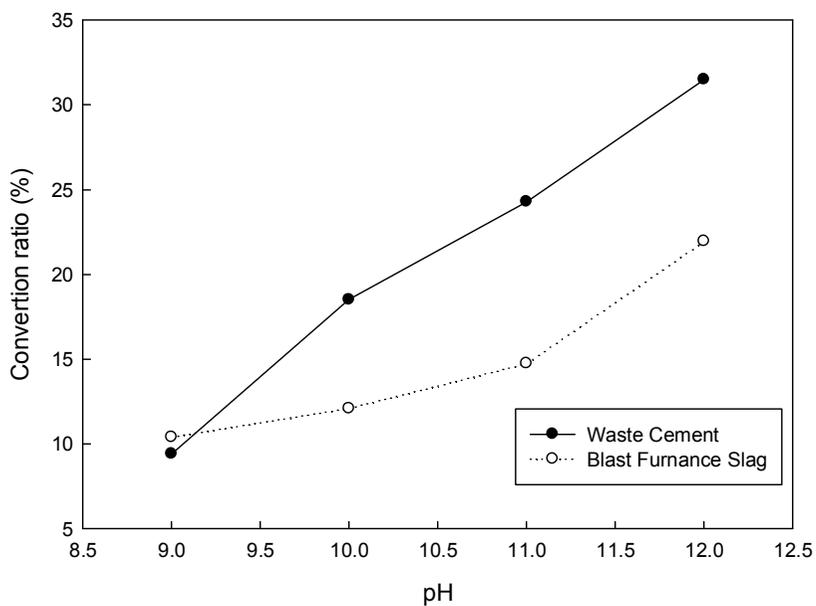
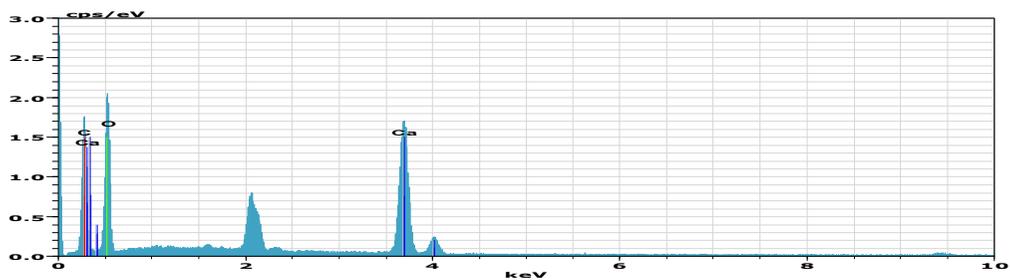
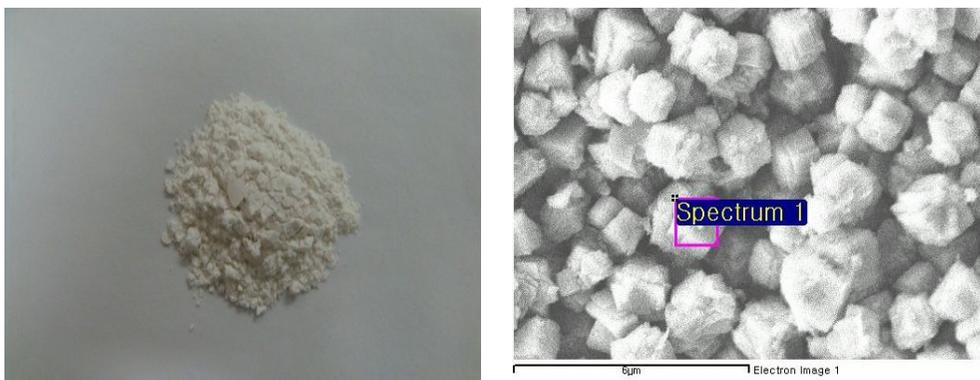


Figure 4-5. Conversion ratio during carbonation step depending on pH.



Element	O	Ca	C	Totals
Weight %	52.27	39.40	8.34	100

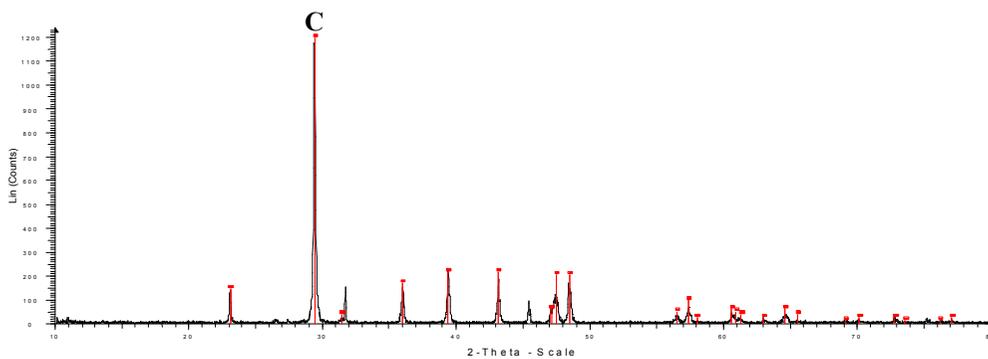
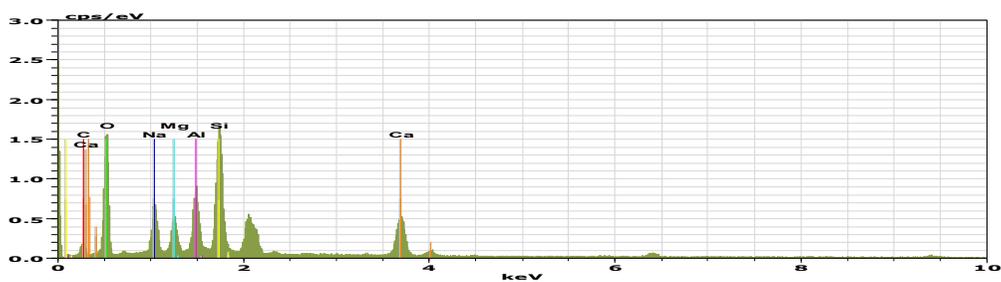
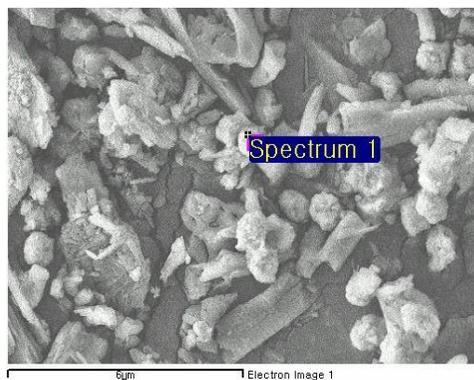
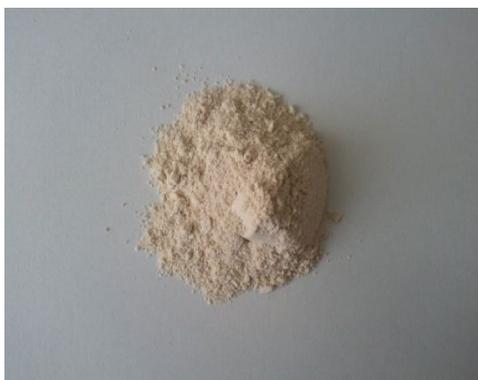


Figure 4-6. SEM-EDS and XRD data obtained for the by-products of waste cement.



Element	O	Ca	C	Na	Mg	Al	Si	Totals
Weight%	57.62	6.96	4.84	5.89	3.56	5.95	12.72	100

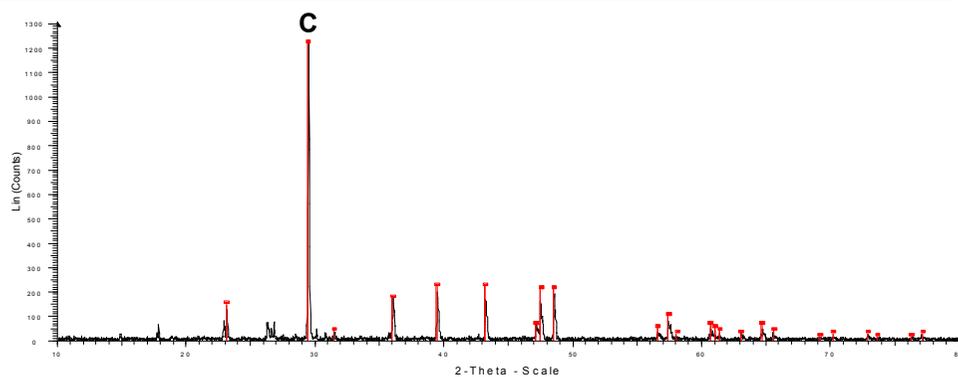


Figure 4-7. SEM-EDS and XRD data obtained for the by-products of blast furnace slag.

4.4. Extraction efficiencies of acids with waste cement

Hydrochloric acid, acetic acid, and ammonium chloride were selected in order to compare their extraction efficiencies. EDTA improved the extraction rate but could not reduce the usage of caustic reagent during the carbonation step. This is very expensive and makes it more difficult to recover and recycle the acid used in the leaching step.

All reactions with waste cement were run under the same conditions. Figure 4-8 shows variations in calcium concentration with reaction time, using solutions containing the three acids individually at various concentrations. At an acid concentration of 0.1 M, the maximum calcium concentration in the extraction solution varied little across different acid types (1,900 mg/L for NH_4Cl versus 2,400 mg/L for HCl and CH_3COOH). As the acid concentration increased, more calcium was extracted from waste cement, making the extraction solution richer in calcium. As shown in Figure 4-9, the acid concentrations investigated show a linear relationship with the maximum calcium content of the extraction solution, regardless of acid type. However, the rate of increment depended on the type of acid. When acid concentrations were increased to 0.5 M, the calcium concentrations of HCl and CH_3COOH solutions increased more than five-fold (~13,000 mg/L), whereas that of NH_4Cl increased threefold (~6,700 mg/L). If all calcium in

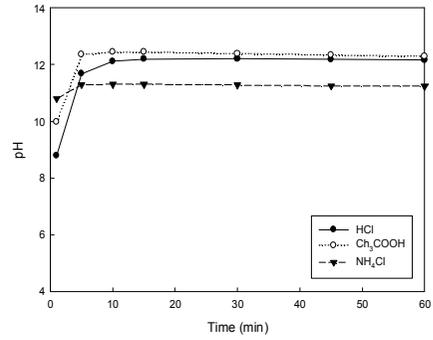
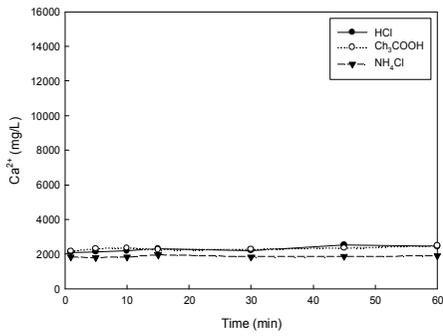
the extraction solution were completely reacted with carbon dioxide, NH_4Cl could take up as much as 0.1 kg CO_2/kg from cement while HCl and CH_3COOH could adsorb 0.2 kg CO_2/kg cement.

The final equilibrium pH values of the extraction step were 8.65, 8.55, and 9.36 for HCl , CH_3COOH , and NH_4Cl solutions, respectively. The degree of extraction therefore seems to be related to the acidity of the extraction solution. To better understand the chemical reaction involved in the extraction and carbonation of waste cement with CO_2 , thermodynamic analysis was conducted with the aid of PHREEQC. This will be discussed further in Chapter 5.

Table 4-4 lists the concentrations of all ions in the final extraction solutions using 0.5 M acids. When acid concentration was increased to 0.5 M, calcium constituted more than 99% of the extracted ions in all cases, indicating that calcium carbonate of high purity could be obtained through the carbonation process. Since the solution was within a pH range of 8–10.5, extraction of calcium ions could easily fall within this pH region, and the calcium concentration in all acids was high.

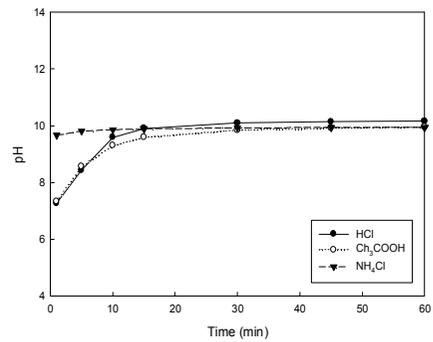
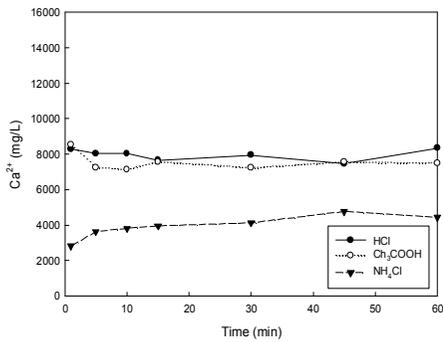
Table 4-5. Composition of the extraction solution from waste cement after one hour.

Component (mg/L)	0.5 M HCl	0.5 M CH₃COOH	0.5 M NH₄Cl
Ca	13670	13220	6733
Si	19.01	33.6	7.209
Mg	219	92.06	8.777
Al	0.00	0.00	0.00
Fe	0.00	0.00	0.00



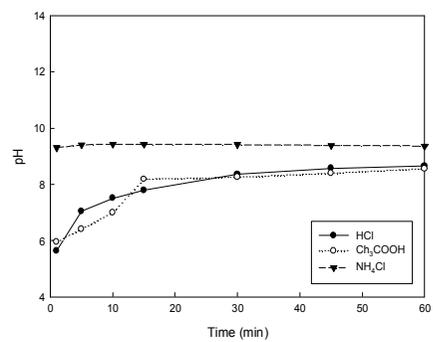
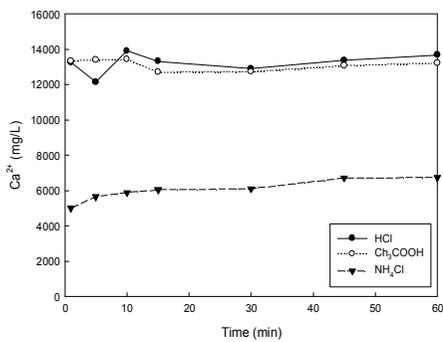
(a) Amount of calcium in solution with 0.1M.

(b) pH of solutions after dissolution with 0.1M.



(c) Amount of calcium in solution with 0.3M.

(d) pH of solutions after dissolution with 0.3M.



(e) Amount of calcium in solution with 0.5M.

(f) pH of solutions after dissolution with 0.5M.

Figure 4-8. Effect of the dissolution of waste cement in the case of each acid.

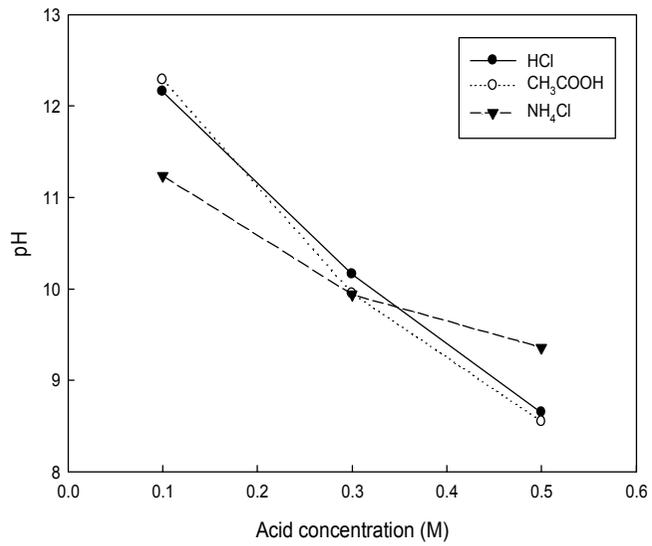
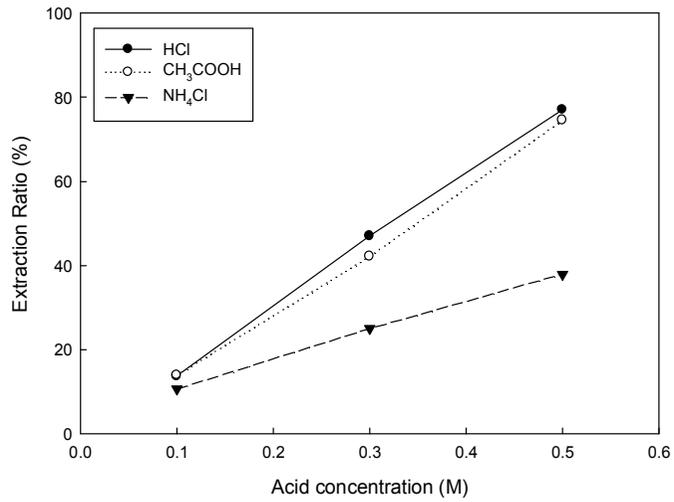


Figure 4-9. Ratio of calcium extraction and pH of extraction solution according to acid concentration.

4.5 Production of calcium carbonate from waste cement

After extraction, the solid residue was separated by filtration and the filtrate reacted with 99.9% CO_2 . The extraction solution of HCl and CH_3COOH did not produce CaCO_3 after injection of CO_2 because the solution pH rapidly declined to acidic conditions. It was therefore necessary to adjust the pH by adding NaOH to induce effective carbonation. However, using the NH_4Cl extraction solution, carbonation was possible without the addition of basic reagents. Moreover, NH_4Cl is regenerated during carbonation. This route may therefore be more economical, although the NH_4Cl solution showed lower Ca content than the HCl and CH_3COOH solutions, under the same conditions. The extent of carbonation calculated from the reduction in the calcium concentration was 70%, i.e., between that obtained using other acids at pH 10 (50%) and pH 12 (95%). NaOH was added to these acidic solutions to adjust the pH and induce carbonation. Consequentially, NH_4Cl took up 0.07 kg CO_2 /kg cement, whereas HCl and CH_3COOH absorbed 0.19 kg CO_2 /kg cement. Although NH_4Cl showed lower maximum capacity for mineral sequestration of CO_2 than hydrochloric and acetic acids, its result was reasonable when compared with others (Bobicki et al., 2012).

After completion of the carbonation stage, the pH of the solution stabilized at 6.1, similar to the initial pH of the NH_4Cl solution used for Ca extraction from waste cement. This solution could therefore be reused for Ca extraction after recovering the precipitated calcium carbonates by filtration.

In order to evaluate the reusability of the recovered NH_4Cl solution, additional tests were performed in a cyclical manner using 1 M NH_4Cl to ensure sufficient Ca extraction, as shown in Fig. 4-10. The calcium content of the extraction solution after the first extraction step was approximately 7000 mg/L, which declined to 2,000 mg/L after carbonation (70% conversion by precipitation). After completion of the first cycle, calcium extraction was achieved from the reaction between a fresh batch of waste cement and the recovered NH_4Cl solution. The calcium concentration in the extraction solution increased to 7,500 mg/L, indicating the extraction of an additional 5,500 mg of calcium. After completing the second carbonation cycle, the calcium concentration declined to 3,700 mg/L, corresponding to 50% conversion by precipitation. In the third cycle, the calcium concentration increased to 9,000 mg/L in the extraction stage, and subsequently decreased to 5,500 mg/L after carbonation, corresponding to 40% conversion by precipitation. This indicates that calcium ions continue to accumulate in the recovered NH_4Cl solution and that conversion efficiency

declines with increasing number of cycles. It may therefore be necessary to remove residual calcium ions at some point during recycling.

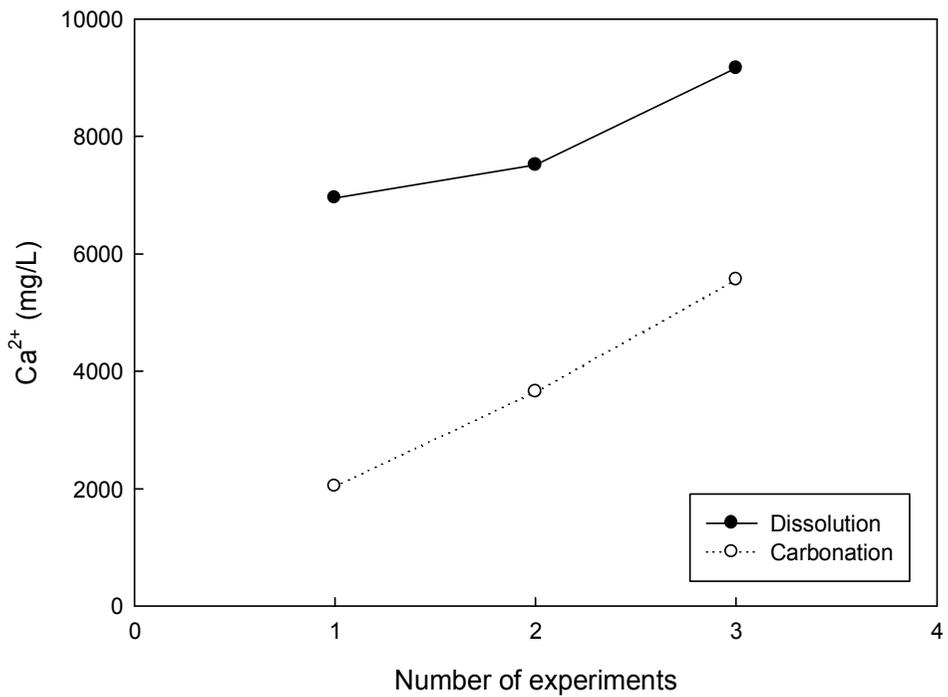
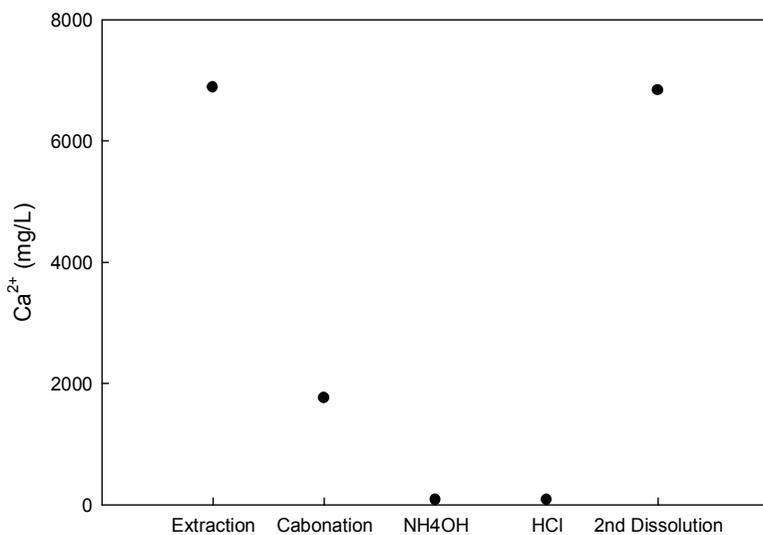


Figure 4-10. Change in Ca^{2+} ion concentration in solution used for repeated cycles of dissolution and carbonation.

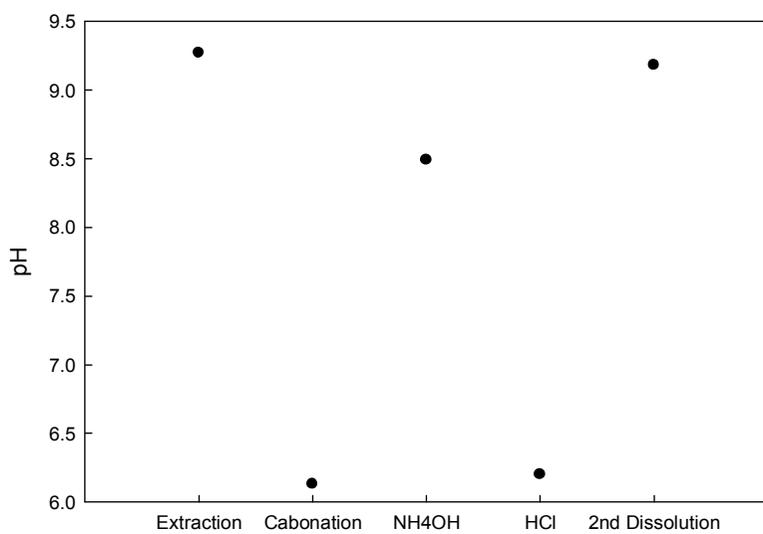
One method used to accomplish this was to increase pH during the carbonation step in order to induce carbonation of residual calcium ions. Figure 4-11 shows the result of such an attempt, in which the addition of ammonium hydroxide after the carbonation step resulted in complete removal of residual calcium ions from the recovered NH_4Cl solution. However, by doing so, the pH of the NH_4Cl solution changed to 6.2–8.5, requiring the addition of acidic reagents such as HCl to bring the pH back to the initial value of 6.2 in order to reuse the solution for Ca extraction. This practice restored the system to the original state and prepared the system to restart a new series of extraction-carbonation cycles.

Figure 4-12 shows XRD and FE-SEM characteristics of the solids obtained from carbonate precipitation of the three acid extracts. When waste cement was dissolved with hydrochloric (Figure 4-11a) and acetic acids (Figure 4-11b), the precipitated solids were pure calcites. However, in the case of ammonium chloride extraction, flower-like particles were observed. XRD analysis revealed that these particles were vaterite. Vaterite is the least thermodynamically stable polymorph of CaCO_3 and has been of great interest due to its medical and industrial applications (Fuchigami et al., 2009; Hadiko et al., 2005). Various experimental conditions have therefore been investigated to promote vaterite synthesis. In particular, it was reported that a

flower-like vaterite could be synthesized when ammonia was present in the carbonate solution (Hu et al., 2012). This may explain the formation of vaterite from the NH_4Cl extraction solution, since NH_3 is generated under this condition. Since vaterite is of higher commercial value than the more common calcite, NH_4Cl extraction has another advantage over other forms of acid extraction.

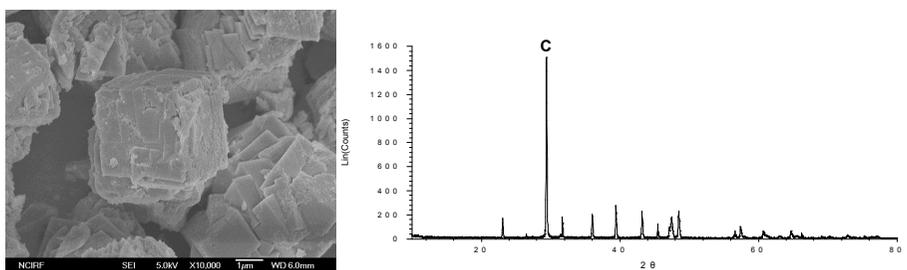


(a) Calcium concentration after each process

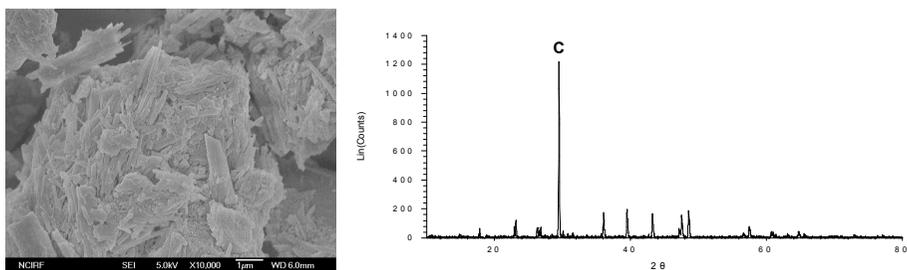


(b) pH of solution after each process

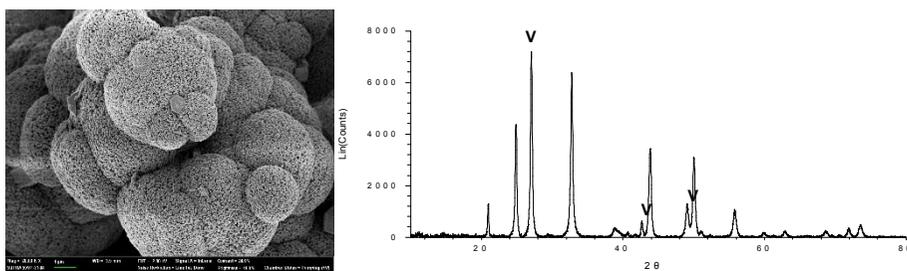
Figure 4-11. Variation in (a) calcium concentration and (b) pH, with carbonation, NH₄OH, and HCl.



(a) HCl



(b) CH₃COOH



(c) NH₄Cl

Figure 4-12. FE-SEM image and XRD data obtained for the by-products of the acid treatments.

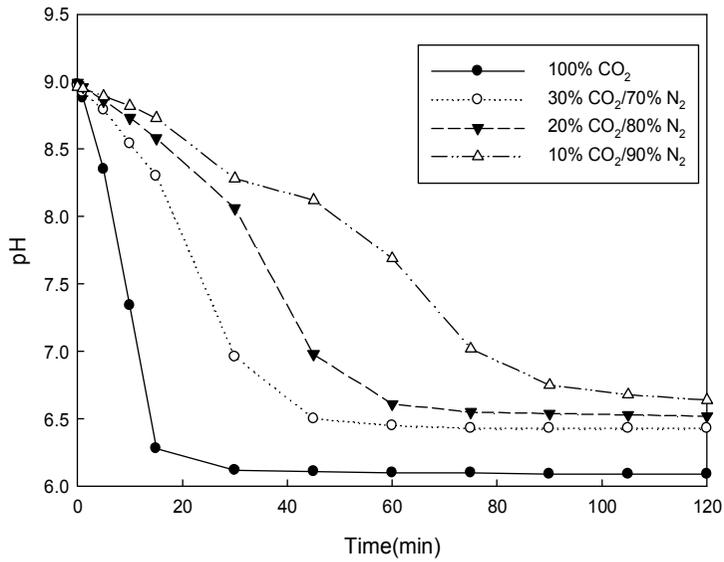
4.6 Carbonation properties with flue gas

The direct treatment of flue gas for carbonation would eliminate the costly carbon capture process, thereby considerably reducing the cost of CCS. This study therefore investigated direct carbonation of flue gas by reacting synthetic flue gases (mixtures of CO_2/N_2 and $\text{CO}_2/\text{N}_2/\text{SO}_x/\text{NO}_x$) with a NH_4Cl solution. Figure 3-13a shows the pH of the solution measured over time when reacted with a mixture of N_2 and CO_2 . As the proportion of CO_2 in the mixtures decreased, the pH of the solution decreased more slowly with time, and it took longer to reach equilibrium. In addition, final pH increased with decreasing CO_2 content in the gas mixtures. Accordingly, the amount of precipitated CaCO_3 declined as the CO_2 content of the mixture decreased.

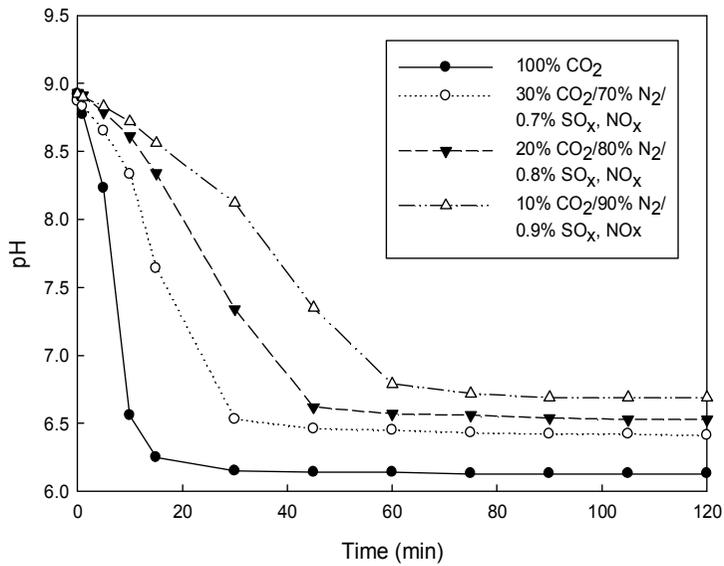
Flue gases from industrial plants may contain small amounts of nitrogen and sulfur oxides. Figure 4-13b shows that the presence of small amounts of SO_x and NO_x (700–900 ppm) in the synthetic gas did not affect carbonation results: equilibrium pH and the amount of precipitated product were very similar to the results obtained without the addition of SO_x and NO_x .

Waste cement was dissolved in NH_4Cl , which would be present as NH_3 and NH_4^+ in water. Ammonia is known to be an efficient substance for capturing carbon dioxide from flue gas (Wang et al., 2011). The ammonia

therefore served to separate carbon dioxide from the gas mixture in carbonation. It is anticipated that NH_4Cl solutions would simultaneously capture and sequester carbon dioxide from real flue gas.



(a) CO₂/N₂



(b) CO₂/N₂/SO_x/NO_x

Figure 4-13. Changes in reaction pH with the virtual flue gas.

Chapter 5 Thermodynamic Analysis

5.1. Fundamental principles

Dissolution and precipitation through the reaction with water can be explained by the law of mass action. In the following the reaction is:



When reaching equilibrium, the following relationship was established:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (23)$$

Here, [] represents the molar concentration of each component, and K is the equilibrium constant affected by temperature changes. If the reactant is a gas, the partial pressure is used as the concentration. The law of mass action is applicable to any reaction, such as the dissolution of minerals, the formation of complexes between dissolved species, and the dissolution of gases in water. K was applied to infinite dilution which was not affected by the other ions in the solution.

However, in the general solution, due to the mutual influence on the concentration of each component as concentrations shift, the molar fraction is the same but K will change. K is expressed as activity, with

thermodynamic concentration in solution; this is dimensionless as the fraction is relative to the standard state:

$$[i] = r_i \cdot m_i / m_i^0 \equiv r_i \cdot m_i \quad (24)$$

where: $[i]$ is the activity of ion i (dimensionless), r_i is the activity coefficient (dimensionless), m_i is the molality (mol/kg H₂O), and m_i^0 is the standard state (1 mol/kg H₂O). The activity coefficient varies by ion, but if only ion i is present, r_i becomes 1. The activity coefficient also varies according to ionic strength, and could be calculated via the Debye-Hückel theory. Ionic strength is described as the number of electrical charges in the solution:

$$I = 1/2 \sum \left(\frac{m_i}{m_i^0} \cdot z_i^2 \right) \equiv 1/2 \sum m_i \cdot z_i^2 \quad (25)$$

where z_i is the charge number of ion i , and m_i is the molality of i . Similar to activity, ionic strength is dimensionless. In the case of pure water, ionic strength is normally less than 0.02, whereas that of seawater is approximately 0.7. In the high salinity (briny) water of the Dead Sea, ionic strength would be 9.4.

If ionic strength is less than 0.1, the Debye-Hückel equation describes the electrostatic interactions:

$$\log r_i = - \frac{Az_i^2\sqrt{I}}{1 + B\tilde{a}_i\sqrt{I}} \quad (26)$$

where A and B are constants depending on temperature, $A = 0.5085$ and $B = 0.3285 \times 10^{10} / \text{m}$ at 25°C ; \hat{a}_i , an empirical ion-size parameter, is obtained by measuring the diameter of the hydrated ions. Table 5-1 shows the value \hat{a}_i of major ions, which indicates the number of water molecules surrounding the ion. A smaller value of \hat{a} means that oppositely charged ions can easily come close and shield it, such that the activity coefficient will eventually be reduced.

In cases where ionic strength is greater than 0.1, Truesdell and Jones derived the activity coefficient from a modified Debye-Hückel equation.

$$\log r_i = -\frac{Az_i^2\sqrt{I}}{1 + Ba_i\sqrt{I}} + b_iI \quad (27)$$

where A and B are the same factor as in the Debye-Hückel equation, and a_i and b_i are ion-specific fit parameters. The value of a_i is modified by the ion-size parameter \hat{a} (see Table 5-2).

Table 5-1. The ion-size parameter, \AA , in the Debye-Hückel equation; numbers are given in Ångstrom (10^{-10} m).

$\text{\AA}/(10^{-10} \text{ m})$	Ion
2.5	Rb^+ , Cs^+ , NH_4^+ , Tl^+ , Ag^+
3.0	K^+ , Cl^- , Br^- , I^- , NO_3^-
3.5	OH^- , F^- , HS^- , BrO_3^- , IO_4^- , MnO_4^-
4.0-4.5	Na^+ , HCO_3^- , H_2PO_4^- , HSO_3^- , Hg_2^{2+} , SO_4^{2-} , SeO_4^{2-} , CrO_4^{2-} , HPO_4^{2-} , PO_4^{3-}
4.5	Pb^{2+} , CO_3^{2-} , SO_3^{2-} , MoO_4^{2-}
5.0	Sr^{2+} , Ba^{2+} , Ra^{2+} , Cd^{2+} , Hg^{2+} , S^{2-} , WO_4^{2-}
6	I^+ , Ca^{2+} , Cu^{2+} , Zn^{2+} , Sn^{2+} , Mn^{2+} , Fe^{2+} , Ni^{2+} , Co^{2+}
8	Mg^{2+} , Be^{2+}
9	H^+ , Al^{3+} , Cr^{3+} , trivalent rare earths
11	Th^{4+} , Zr^{4+} , Ce^{4+} , Sn^{4+}

Table 5-2. Individual ion activity coefficient parameters in the Truesdell and Jones equation.

Ion	a / (10⁻¹⁰m)	b
Na ⁺	4.0	0.075
K ⁺	3.5	0.015
Mg ²⁺	5.5	0.20
Ca ²⁺	5.0	0.165
Cl ⁻	3.5	0.015
HCO ₃	5.4	0.0
CO ₃ ²⁻	5.4	0.0
SO ₄ ²⁻	5.0	-0.04

The lines in Figure 5-1 correspond to the Truesdell and Jones equation. At low ionic strength they agree well with the values obtained with the Debye-Hückel equation. At high ionic strength the activity coefficients of cations are seen to increase by the action of the term (b_i·I). The Truesdell and Jones equation is a reasonable approximation up to I values of about two in dominantly chloride solutions. The Davies equation is another relation often used to calculate activity coefficients and is applicable up to an ionic strength of about five.

$$\log r_i = -Az_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (28)$$

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where A is the same temperature dependent coefficient as in Equation (26).

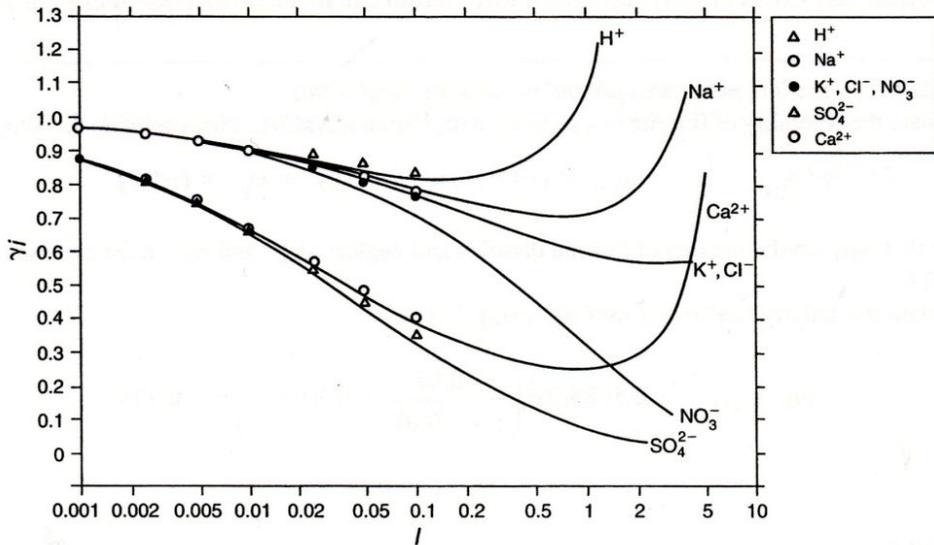
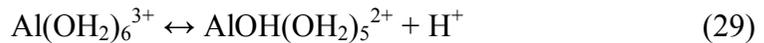


Figure 5-1. Activity coefficients for some ions as a function of ionic strength; symbols represent calculations with the Debye-Hückel equation, while lines correspond to the Truesdell and Jones Equation.

In aqueous solution, ions may become attached to each other as ion pairs or aqueous complexes. There are major complexes (CaSO_4^0 , CaF^+ , or CaOH^+), heavy metals (CdCl^+ , HgCl_3^- , or PbOH^+), and heavy complexes with an organic ligand (CuC_2O_4). The complexes may be outer sphere, with water molecules present in between the constituent ions of the complex, or inner sphere, when a covalent bond is formed and water molecules that

surround the ions have been expelled. These sphere states are gradual and fluctuate over time.

Complexation will lower the activity of the free ion in water, and increase the solubility of minerals and the mobility of trace metals. The majority of complexes consist of a metal cation, surrounded by a number of ligands. For example, Al^{3+} in water is surrounded by six water molecules to form the octahedral shaped complex $\text{Al}(\text{OH}_2)_6^{3+}$. Depending on pH, protons are released from the complex and its charge increases:



The formation of aqueous complexes can be described by equilibria of the type:



The distribution of the species is obtained by applying the law of mass action:

$$K = \frac{[\text{CaSO}_4^0]}{[\text{Ca}^{2+}][\text{SO}_4^{2-}]} = 10^{2.5} \quad (31)$$

The reaction is written as an ion-association reaction and the corresponding mass action constant is therefore termed a stability constant. Sometimes equilibria for aqueous complexes are written as dissociation reactions and the dissociation constant for the CaSO_4^0 complex is obviously the inverse of equation (30).

Both aqueous complexing and activity coefficients will lower the activity of the free ions, and their combined effect must be calculated. The total amount of Ca^{2+} in solution is given by a mass balance equation comprising the various aqueous complexes of Ca^{2+} , given in molar units:

$$\sum C_a = m_{\text{Ca}^{2+}} + m_{\text{CaSO}_4} + m_{\text{CaOH}^+} + \dots \quad (32)$$

A similar mass balance equation can be written for all other substances in solution. In order to calculate the activity of $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$, we have to solve a set of mass balance equations, with concentrations in molar units, and a set of mass action equations, with concentrations expressed as activities. The calculation proceeds through an interactive procedure. Activity coefficients and ion activities are first calculated from the analytical data, with these used to calculate activities of complexes. The molar concentrations of complexes are then obtained, enabling calculation of improved mass balances and a better estimate of ionic strength. This procedure continues until no further significant improvement is obtained.

The methods described here work well for electrolyte solutions of ionic strength of up to about seawater ($I = 0.7$), or up to $I = 2$ mol/L when HCO_3^- and SO_4^{2-} concentrations are low. For more concentrated solutions, other methods are available. The so-called Pitzer equations, in particular, have

been successful in describing mineral equilibria in highly concentrated solutions.

Once the activities of free ions in solution are calculated, the state of saturation of water with respect to minerals is also calculated. One way to do this is to compare the solubility product K with the analogue product of the activities derived from water analyses. This is often termed the Ion Activity Product (IAP). For example for gypsum:

$$K_{gypsum} = [Ca^{2+}] [SO_4^{2-}] \quad (\text{activities at equilibrium})$$

and

$$IAP_{gypsum} = [Ca^{2+}][SO_4^{2-}] \quad (\text{activities in water sample})$$

Saturation conditions may also be expressed as the ratio between IAP and K , or the saturation state Ω :

$$\Omega = \frac{IAP}{K} \quad (33)$$

Thus, when $\Omega = 1$ there is equilibrium; $\Omega > 1$ indicates super saturation and $\Omega < 1$ indicates sub saturation. For larger deviations from equilibrium, a logarithmic scale can be useful and is given by the saturation index SI:

$$SI = \log (IAP/K) \quad (34)$$

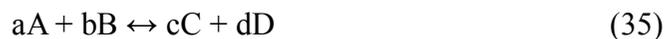
For $SI = 0$, there is equilibrium between the mineral and the solution; $SI < 0$ reflects sub saturation, and $SI > 0$ reflects super saturation. For comparison

purposes, it can be useful to normalize Ω and SI to the number of solutes v in the ion activity product, i.e., $v = 2$ for CaCO_3 (calcite) and $v = 4$ for $\text{CaMg}(\text{CO}_3)_2$ (dolomite). The saturation state then becomes $\Omega^{1/v}$ and the saturation index is SI/v .

Different types of information can be obtained from saturation data. In a few cases, an actual control of solutes by equilibrium with a mineral can be clearly demonstrated. Often there is no equilibrium, and in these cases, the saturation state merely indicates in which direction the processes may proceed; for sub saturation dissolution is expected, while super saturation suggests precipitation.

Thermodynamics is the science concerned with energy distribution among substances in a system. It offers an impressive framework of formulae, which can be derived from a few basic laws. An introduction to thermodynamics can be found elsewhere. Here we limit ourselves to some practical aspects and in particular to the calculation of mass action constants and their dependency on temperature from thermodynamic tabulations.

For the general reaction:



we may write:

$$\Delta G_r = \Delta G_r^0 + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (36)$$

where ΔG_r is the change in Gibbs free energy (kJ/mol) of the reaction, ΔG_r^0 is the standard Gibbs free energy of the reaction and equal to ΔG_r when each product or reactant is present at unit activity (so that the log term becomes zero) at a specified standard state (25 °C, 1 atm), [i] denotes the activity of I, R is the gas constant (8.314×10^{-3} kJ/mol/deg), and T is absolute temperature (in Kelvin).

In order texts, energy is often expressed in kcal/mol which can be converted to kJ/mol by multiplying by 4.184 J/cal (hence $R = 1.987 \times 10^{-3}$ kJ/mol/deg). The prefix Δ is used because energy can be measured only as relative amounts. The direction in which the reaction will proceed is indicated by ΔG_r :

$\Delta G_r > 0$ the reaction proceeds to the left;

$\Delta G_r = 0$ the reaction is at equilibrium;

$\Delta G_r < 0$ the reaction proceeds to the right.

In the case of equilibrium, Equation (36) therefore reduces to:

$$\Delta G_r^0 = -RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (37)$$

Note that the activity product in the last term is equal to the mass action constant K:

$$\Delta G_r^0 = -RT \ln K \quad (38)$$

Back substitution of Equation (38) in (36) results in the following:

$$\Delta G_r = -RT \ln K + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (39)$$

In Equation (39), the distance from equilibrium is expressed in terms of the mass action constant and the solution composition, a formulation analogous to the saturation index SI.

Equation (38) has the practical application that it allows us to calculate the mass action constant for any reaction from tabulated data of ΔG_f^0 for dissolved substances, minerals, and gases. ΔG_f^0 is the free energy of formation, which is the energy needed to produce one mole of a substance from pure elements in their most stable form. The latter have, by definition, zero values. Tabulations are normally given for 25 °C and 1 atm. ΔG_f^0 is calculated from:

$$\Delta G_r^0 = \sum \Delta G_f^0_{products} - \sum \Delta G_f^0_{reactants} \quad (40)$$

A number of complications of thermodynamic data concerning mineral-water systems are available. Consistent sets of data should preferably be used as erratic values may otherwise be obtained. For example, the listed $\Delta G_f^0_{\text{calcite}}$ could have been calculated from solubility measurements using values $\Delta G_f^0_{\text{Ca}^{2+}}$ and $\Delta G_f^0_{\text{CO}_3^{2-}}$. When K_{calcite} is subsequently calculated

from thermodynamic tables with a different $\Delta G_{f, \text{CO}_3^{2-}}^0$ value, the result will clearly be erroneous. Even when these precautions are taken, one discovers that different compilations may give slightly different constants. For example, the value of K_{calcite} is slightly higher than the currently accepted value of $10^{-8.48}$, which includes corrections for aqueous complexes.

If the reaction speed is high, equilibrium is sufficient to explain how the dissolution or growth of minerals proceeds. When the reaction rate is slow, it is not only the equilibrium state that is important, but also the rate at which equilibrium is reached. The reaction rate includes the transport of solutes between the bulk solution and the mineral surface, the ad- and desorption of solutes at the surface, hydration and dehydration of ions and surface migration. Three reactions must occur simultaneously but some may become slower or faster depending on conditions. Since the overall rate will be determined by the slowest reaction rate, it is important to identify the rate limiting process. In the case of the solubility of minerals, this appears to be the dissolution mechanism. Table 5-3 shows the reaction step to determine the overall reaction rate, with solubility corresponding to the minerals. Calcium carbonate may determine the overall reaction rate of the surface reaction ($6 \cdot 10^{-5} \text{ mol/L}$) because it has low solubility. In this study, it was therefore necessary to consider both the reaction rate and equilibrium.

It is possible to show the relationship between the concentration and reaction rate using the rate equation.

$$R = k \frac{A_0}{V} \left(\frac{m}{m_0} \right)^n g(C) \quad (41)$$

where R is the overall reaction rate (mol/L/s), k is the specific rate (mol/m²/s), A₀ is the initial surface area of the solid (m²), V is the volume of solution (m³), m₀ is the initial moles of solid, and m is the moles of solid at a given time. The overall rate of the initial stage is influenced by the specific rate (k) and the ratio of surface area (A₀) to volume of the solution (V). The reaction is affected by changes in the factor (m/m₀)ⁿ during dissolution. The factor (n) for the ratio of surface area to volume is 2/3 for a mono-dispersed population of dissolving or growing spheres and cubes, because m is proportional to r³ (here r is the radius of the sphere or the side of the cube) while the surface is proportional to r². If poly-dispersed crystals are reacted, n will increase up to 3.4 according to the particle size distribution. The g(C) is a factor including the effect of the solution composition on the rate, which is also affected by pH, distance from equilibrium, and the effects of catalysis and inhibition.

Table 5-3. Rate controlling dissolution mechanism and solubility for various substances.

Substance	Solubility	Dissolution rate control
Ca ₅ (PO ₄) ₃ OH	2 · 10 ⁻⁸	Surface-reaction
KAlSi ₃ O ₈	3 · 10 ⁻⁷	Surface-reaction
NaAlSi ₃ O ₈	6 · 10 ⁻⁷	Surface-reaction
BaSO ₄	1 · 10 ⁻⁵	Surface-reaction
AgCl	1 · 10 ⁻⁵	Transport
SrCO ₃	3 · 10 ⁻⁵	Surface-reaction
CaCO ₃	6 · 10 ⁻⁵	Surface-reaction
Ag ₂ CrO ₄	1 · 10 ⁻⁴	Surface-reaction
PbSO ₄	1 · 10 ⁻⁴	Mixed
Ba(IO ₃) ₂	8 · 10 ⁻⁴	Transport
SrSO ₄	9 · 10 ⁻⁴	Surface-reaction
Opaline SiO ₄	2 · 10 ⁻³	Surface-reaction
CaSO ₄ · 2H ₂ O	5 · 10 ⁻³	Transport
Na ₂ SO ₄ · 10H ₂ O	2 · 10 ⁻¹	Transport
MgSO ₄ · 7H ₂ O	3 · 10 ⁰	Transport
Na ₂ CO ₃ · 10H ₂ O	3 · 10 ⁰	Transport
KCl	4 · 10 ⁰	Transport
NaCl	5 · 10 ⁰	Transport
MgCl ₂ · 6H ₂ O	5 · 10 ⁰	Transport

5.2. Definition of the mineralogical phases of waste cement

For the simulation, it is first necessary to define the mineralogical phases of the starting material. Ordinary Portland Cement (OPC) generally consists of calcium silicates (Ca_3SiO_5 and Ca_2SiO_4), aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$), and ferrite ($\text{Ca}_4(\text{Al}_x\text{Fe}_{1-x})_4\text{O}_{10}$). These components react with water to form hydration products such as amorphous CSH (calcium silicate hydrate), portlandite, and ettringite. XRD analysis of the studied material allowed identification of the following crystalline constituents: portlandite, calcite, quartz, albite, microcline, and ettringite. However, it is difficult to determine the amounts of different phases analytically since XRD only shows materials with crystalline structures. The amount of amorphous CSH was therefore determined using thermo-gravimetric analysis (TGA). Figure 5-2 shows the results of TGA. Abrupt weight loss at approximately 450 °C is associated with the dehydration of portlandite; weight loss occurring between 700–800 °C relates to the decomposition of calcium carbonate, and continuous weight loss over the entire range from 105–500 °C is due to the dehydration of calcium silicate hydrates (March et al., 1988). When the weight loss in each region was calculated, the contents of CSH and portlandite were estimated to be 4.9% and 5.6%, respectively. The content of portlandite was compared with XRD results and normalized to estimate the composition of

the sample, as shown in Table 5-4. CSH composition was assumed to be $\text{Ca}_{1.8}\text{SiO}_{3.8}\text{H}_2\text{O}$, which was found to be a good approximation for modeling concrete leaching (Schiopu et al., 2009).

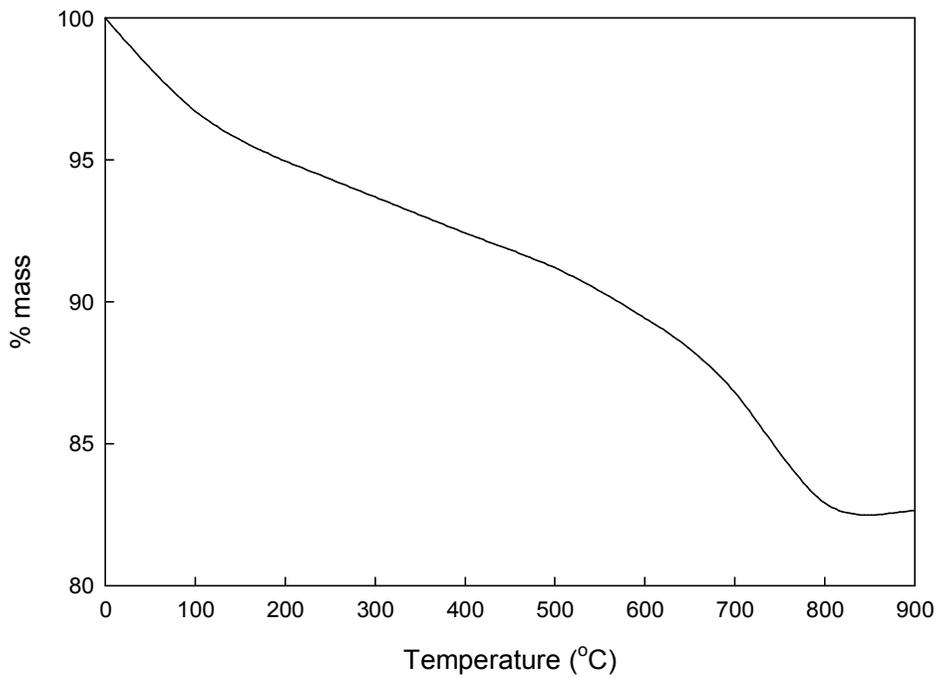


Figure 5-2. TGA results of waste cement sample.

Table 5-4. Constituent minerals of cements as determined by XRD, and by combining TGA and XRD.

Compound	XRD		TGA and XRD	
	wt%	mole	wt%	mole
CSH-gel-1.8	-	-	9.48	0.053
Albite	11.2	0.042	10.13	0.038
Anhydrite	3.77	0.027	3.41	0.025
Calcite	17.37	0.173	15.72	0.157
Ettringite	9.04	0.007	8.18	0.006
Microcline	19.32	0.069	17.48	0.062
Portlandite	12.05	0.162	10.90	0.147
Quartz	27.25	0.453	24.66	0.410

The hydrolysis equilibrium constants of quartz, calcite, microcline, and albite were estimated using the PHREEQC databases. However, CSH, portlandite, and anhydrite were not included in the PHREEQC database, and therefore appropriate values were obtained from the literature (Schiopu et al., 2009, Lothenbach et al., 2008) and added to the database. The expected secondary carbonate mineral assemblage due to CO₂ gas injection at 1 atm was based on the PHREEQC database. Table 5-5 gives the complete list of

initial and newly formed phases with their stoichiometry reactions and equilibrium constants. Assuming that all reactions reached equilibrium, extraction and carbonation were calculated via the EQUILIBRIUM _PHASES statement.

Table 5-5. Phases to be involved in the reaction.

Mineralogical phase	Stoichiometry reaction	Equilibrium
		Constant (log K)
CSH-gel-1.8	$\text{Ca}_{1.8}\text{SiO}_{3.8} \cdot \text{H}_2\text{O} + 3.6\text{H}^+ + 2\text{H}_2\text{O}$	32.7
	$= 1.8\text{Ca}^{+2} + 0.8\text{H}_2\text{O} + 2\text{H}_2\text{O} + \text{H}_4\text{SiO}_4$	
Albite	$\text{NaAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} = \text{Na}^+ + \text{Al}(\text{OH})_4^-$	-18.002
	$+ 3 \text{H}_4\text{SiO}_4$	
Anhydrite	$\text{CaSO}_4 = \text{Ca}^{+2} + \text{SO}_4^{-2}$	-4.41
Calcite	$\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{+2} + \text{HCO}_3^-$	1.849
Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O} + 12\text{H}^+$	56.5
	$= 2\text{Al}^{+3} + 3\text{SO}_4^{-2} + 6\text{Ca}^{+2} + 38\text{H}_2\text{O}$	
Microcline	$\text{KAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} = \text{K}^+ + \text{Al}(\text{OH})_4^- +$	-20.573
	$3\text{H}_4\text{SiO}_4$	
Portlandite	$\text{Ca}(\text{OH})_2 = \text{Ca}^{+2} + 2\text{OH}^-$	-5.20
Quartz	$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$	-3.98

5.3. Thermodynamic analysis of extraction efficiencies using PHREEQC

Understanding the chemical reactions involved in any chemical process is important to optimize and control the process variables and parameters. In an actual experiment, derivation of equilibrium or reaction rate is difficult due to complication from various experimental conditions and characteristics of the reactants.

PHREEQC can simulate complex reactions between dissolved gases, aqueous solutions, and minerals (Parkhurst et al., 1999). The geochemical program PHREEQC takes into account the concentration of ions in water, such as calcium, sodium and sulfate, and then calculates the quantities of these ions and minerals dissolved in water. It can also determine whether they will precipitate out of solution to form minerals. The calculations utilize thermodynamic databases that include a wide range of data for mineral phases and compounds. The PHREEQC simulation is also capable of incorporating kinetic equations for chemical reactions and determining speciation at any designated time. We therefore analyzed extraction efficiencies of three acids (hydrochloric, acetic acids and ammonium chloride) with waste cement.

In previous experimental results, these acids showed a high selectivity for calcium in waste cement ($\geq 99\%$). It was expected that calcium would be present mostly in the form of Ca^{2+} , according to the Eh-pH diagram (Figure 5-3).

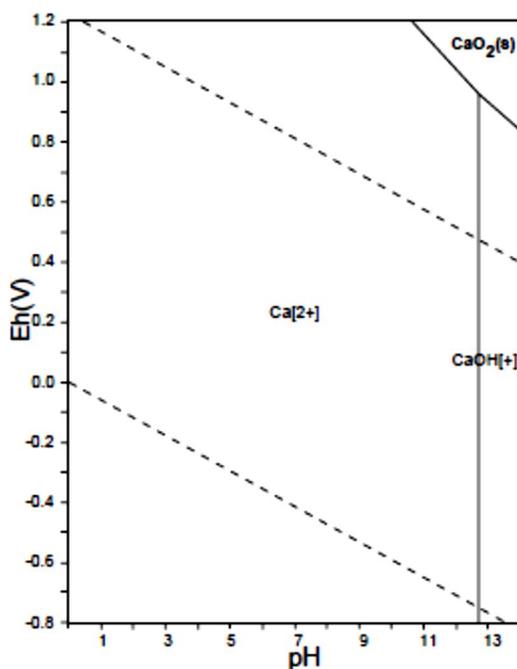
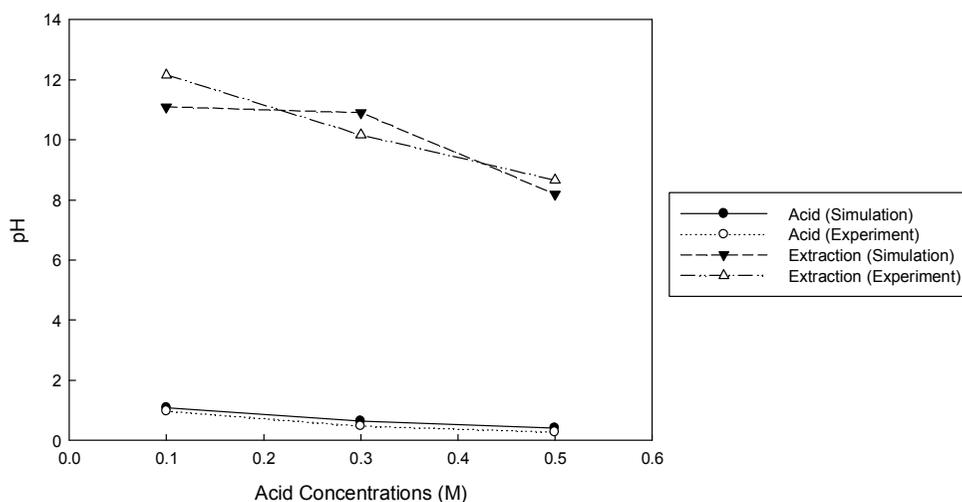


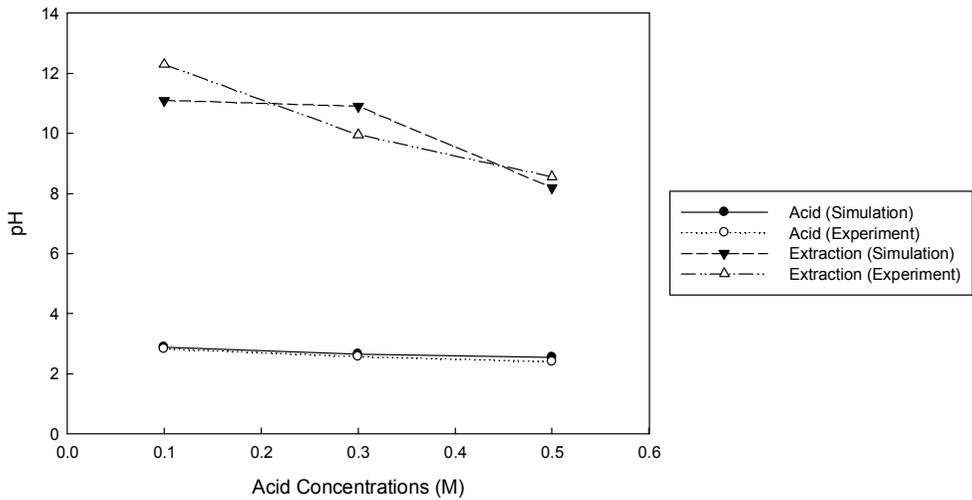
Figure 5-3. Eh-pH diagrams of the system Ca-O-H. $\sum\text{Ca} = 10^{-10}$, 298.15K, 10^5 Pa.

Initial and equilibrium pH extracted by various acids from PHREEQC were compared with experimental results. Since hydrochloric acid is a strong acid, the amount of H^{+} was the same as acid concentration. Figure 5-4a shows that initial pH was at 1.08–0.41, depending on acid concentration

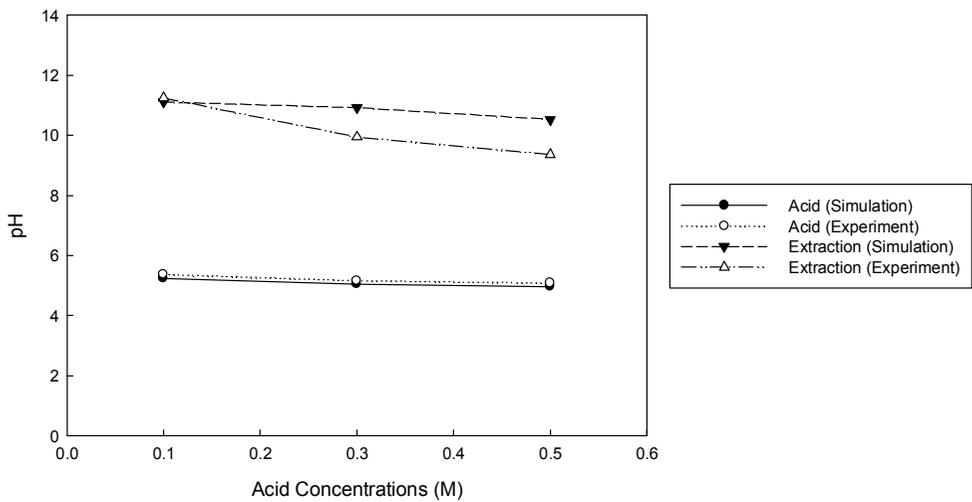
(0.1–0.5M). On the other hand, the dissociation constants of acetic acid and ammonium chloride were 4.75 and 9.24, indicating that not all acid was dissociated into the solution. The pH of these weak acids was therefore 2.8–2.5 and 5.2–4.9, respectively, higher than in the case of hydrochloric acid at the same concentration, as shown in Figures 5-4b and c. These results were similar to those for pH measured experimentally.



(a) Hydrochloric acid



(b) Acetic acid



(c) Ammonium chloride

Figure 5-4. Comparison of simulated and experimental pH (initial and equilibrium) in various acids.

After reacting with waste cement, equilibrium pH showed a similar value across all acids, unlike initial pH that changed in accordance with acid type for the dissociation constant. Hydrochloric and acetic acids, in particular, showed the same value from 11.09 (0.1 M) to 8.19 (0.5 M). Although the type of negative ions and the amount of H^+ were different in these acids, waste cement had high reactivity, generating large amounts of Ca^{2+} at low acid concentration. Ammonium chloride generated NH_4^+ to remain within a range of constant pH (11.10–10.52) with higher value than in the case of other acids.

Figure 5-5 shows the amounts of Ca in various acid concentrations after reactions with cement, with these being smaller than experimental results. Variations became larger as acid concentration increased. However, a similar to the trend for pH, hydrochloric and acetic acids had the same amounts in across all concentrations. Ammonium chloride showed a lower extraction rate, except at 0.1 M.

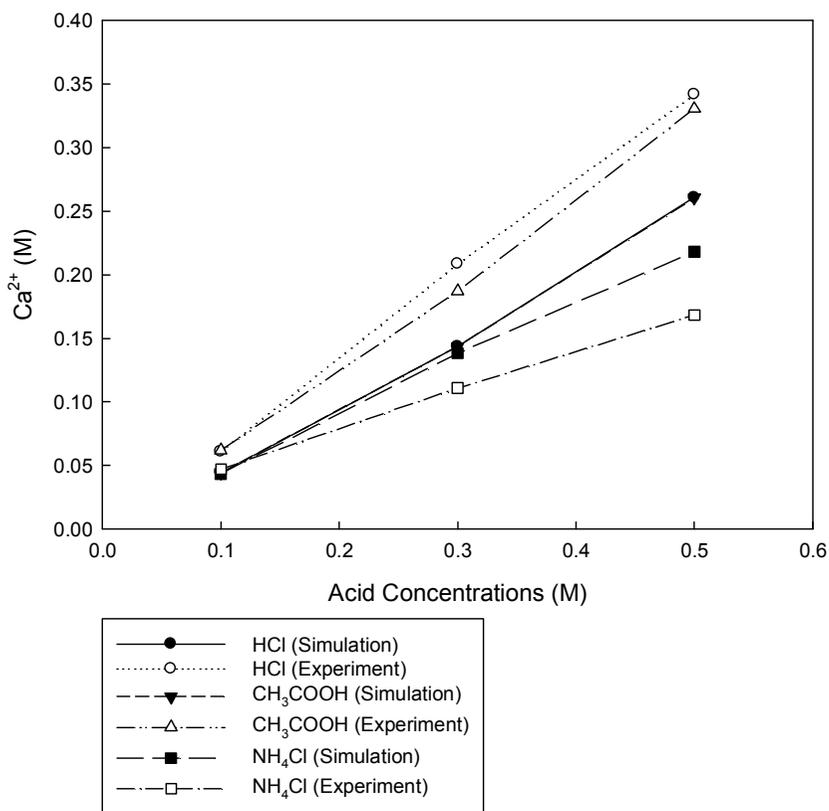


Figure 5-5. Comparison of extraction efficiency of waste cement in various acids.

Although solutions extracted from waste cement had relatively high calcium content, there were also trace elements (e.g. Al, Na and S) that could form other complex salts. In order to evaluate this phenomenon, Table 5-6 lists all elements and species in the extraction solution from simulation, and Table 5-7 shows the quantities of main components in 0.5 M acids. These solutions were rich in Ca, S, Al, and Si, regardless of acid type. Calcium was

present at 93%, which was almost all in Ca^{2+} form, with some in the form of CaOH^+ . S was mainly found as SO_4^{2-} and CaSO_4 , Al was found as $\text{Al}(\text{OH})_4$ and $\text{Al}(\text{OH})_3$, and Si was present as H_3SiO_4^- and H_4SiO_4 . Main species of all elements were the same in the Eh-pH diagram (Figure 5-6). Even though total concentrations of elements in the Eh-pH diagram were very low (10^{-5}M), this could be modified with the Nernst equation for comparison with simulation results:

$$E = E^0 - \frac{0.059}{n} \log \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b} - 0.059 \left(\frac{m}{n} \right) pH \quad (42)$$

The concentration of C or D ions in solution increased, resulting in an increase in the y-intercept. As a result, overall the graph shifted slightly to the left, but this was not a significant change.

Table 5-6. All elements and species in the extraction solution.

Elements	Species
Al	Al(OH)_4^- , Al(OH)_3 , Al(OH)_2^+ , AlOH^{+2} , Al^{+3} , AlSO_4^+ , $\text{Al(SO}_4)_2^-$, AlHSO_4^{+2}
C	CaCO_3 , CO_3^{-2} , NaCO_3^- , HCO_3^- , CaHCO_3^+ , NaHCO_3 , CO_2
Ca	Ca^{+2} , CaOH^+ , CaSO_4 , CaCO_3 , CaHCO_3^+ , CaHSO_4^+
K	K^+ , KSO_4^-
Na	Na^+ , NaSO_4^- , NaCO_3^- , NaHCO_3 , NaOH
S	SO_4^{-2} , CaSO_4 , NaSO_4^- , KSO_4^- , HSO_4^- , CaHSO_4^+ , AlSO_4^+ , $\text{Al(SO}_4)_2^-$, AlHSO_4^{+2}
Si	H_3SiO_4^- , H_4SiO_4 , $\text{H}_2\text{SiO}_4^{-2}$

Table 5-7. Quantities of main components in 0.5 M acids.

Elements & Species	HCl	CH ₃ COOH	NH ₄ Cl
Ca	2.61×10^{-1}	2.61×10^{-1}	2.18×10^{-1}
Ca ⁺²	2.55×10^{-1}	2.55×10^{-1}	2.18×10^{-1}
CaOH ⁺	5.80×10^{-3}	5.80×10^{-3}	3.91×10^{-3}
S(6)	9.38×10^{-3}	9.38×10^{-3}	1.80×10^{-4}
SO ₄ ⁻²	5.80×10^{-3}	5.80×10^{-3}	1.02×10^{-4}
CaSO ₄	3.58×10^{-3}	3.58×10^{-3}	7.07×10^{-5}
Al	7.75×10^{-3}	7.67×10^{-3}	1.08×10^{-4}
Al(OH) ₄ ⁻	7.74×10^{-3}	7.65×10^{-3}	1.08×10^{-4}
Al(OH) ₃	1.42×10^{-5}	1.39×10^{-5}	9.53×10^{-10}
Si	8.92×10^{-5}	8.92×10^{-5}	8.80×10^{-4}
H ₃ SiO ₄ ⁻	8.54×10^{-5}	8.54×10^{-5}	7.90×10^{-4}
H ₄ SiO ₄	3.81×10^{-6}	3.83×10^{-6}	8.46×10^{-5}

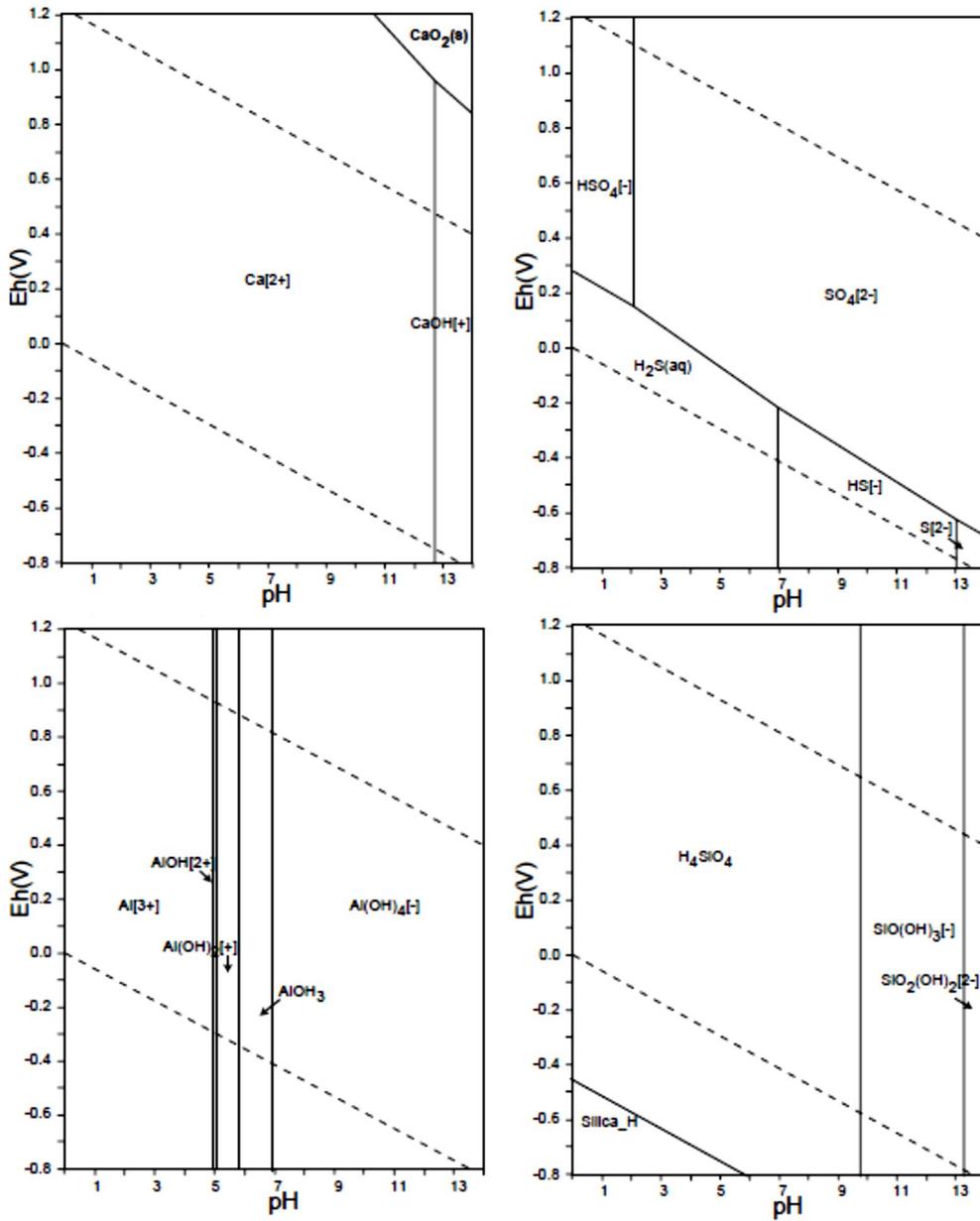


Figure 5-6. Eh-pH diagrams of the system Ca, S, Al, and Si.

5.4. PHREEQC analysis of cyclical mineral carbonation using NH₄Cl solution

In this section, we wanted to determine whether it was feasible to use PHREEQC to represent cyclical MC processes using a NH₄Cl solution. In order to accurately analyze experimental data before the simulation, waste cement was analyzed before and after extraction, together with the resulting solution. Table 5-8 shows moles obtained by converting the XRF analysis results of the cement. Though silica was numerically increased to 41% (from 39% in the XRF results), it is impossible to increase silica by reaction. Other components were calculated by setting the same moles as the original sample of silica as its relative amount increases as the amount of calcium decreases. As a result, calcium decreased from 0.67 M to 0.46 M, but there was little change in other components. It was found that the calcium concentration (0.17M) extracted with 1M NH₄Cl solution was similar to using a reduced amount in waste cement. It was notable that chlorine increased sharply to 0.28 by 0.002 M from ammonium chloride.

Table 5-8. Components of cements before and after dissolution, as analyzed by XRF.

Formula	Raw cement		Residual cement	
	wt%	mole	wt%	mole
SiO ₂	39.1	0.65	41.01	0.65
CaO	37.95	0.67	27.36	0.46
Al ₂ O ₃	9.83	0.09	9.79	0.09
Fe ₂ O ₃	4.98	0.03	4.35	0.02
K ₂ O	2.27	0.02	2.33	0.02
SO ₃	2.08	0.02	0.81	0.009
MgO	1.98	0.04	2.04	0.04
Na ₂ O	0.74	0.01	0.62	0.008
Cl	0.08	0.002	10.72	0.28

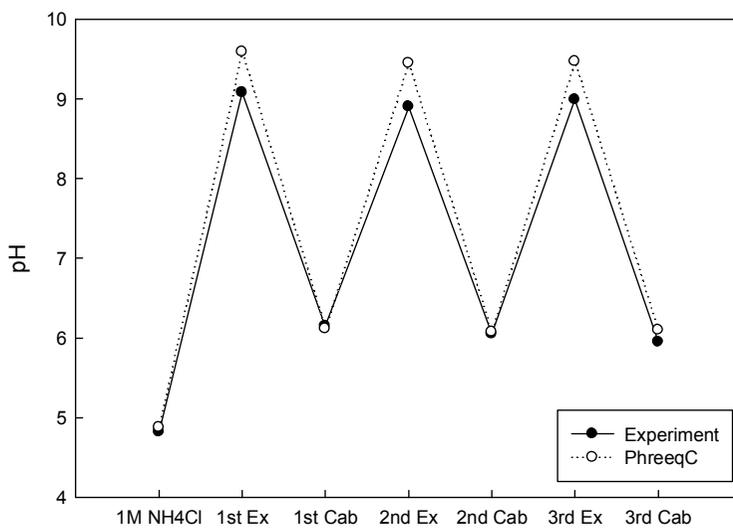
Figure 5-7 shows the pH and the amount of calcium at different stages throughout the extraction and carbonation process. During the first stage of extraction, the amount of calcium estimated by the simulation was 1.3 times higher than experimental results. This indicates that not all of the calcium was extracted from the waste cement particles; this is credible because the

particle core may still remain intact. After the first stage of carbonation by injecting CO₂ into the solution, the simulation showed 95% calcium removal from the solution by precipitation, whereas in the experiment, only 70% of the calcium was removed.

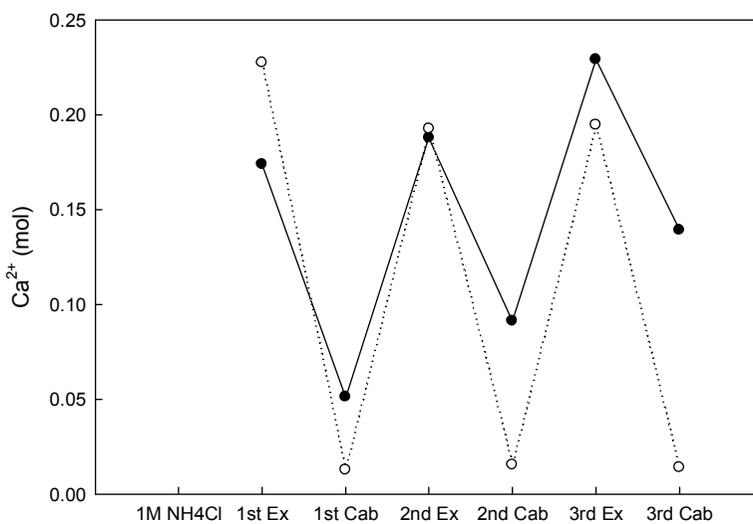
In the subsequent extraction and precipitation cycles, the simulation results showed that the amount of Ca in solution fluctuates within a range of fixed values, in a periodic fashion. On the other hand, experimental results showed that the amount of Ca present after the precipitation step increased with each cycle. Correspondingly, the maximum amount of Ca remaining after extraction also increased with each cycle. There are two possible reasons for these deviations: (1) kinetics, and (2) lack of thermo-dynamic data for the formation of different types of calcium carbonate polymorphs, requiring further study.

One reason for such a phenomenon is the kinetic/thermodynamic balance as controlled by the amount of Ca²⁺ and CO₂ present in the solution. Calcium carbonate can occur in the form of three anhydrous crystalline polymorphs: vaterite, aragonite, and calcite. Vaterite is unstable under standard conditions and transforms easily into aragonite or calcite when in contact with water. However, under specific conditions, vaterite forms and persists without transforming. It was reported that vaterite particles were obtained within a

very narrow region of Ca^{2+} and CO_2 concentrations at a pH from 9.3 to 9.9 (Brecevic et al., 2007). Furthermore, it was reported that the correlation between pCO_2 and Ca^{2+} was one of the most important factors in determining the calcium carbonate precipitation reaction (Dickinson et al., 2002). When these were in complete balance, calcite formed; if the balance slightly favored pCO_2 , vaterite formation was induced but CaCO_3 precipitation was kinetically controlled. The precipitation conditions under which the current investigation was conducted were within the aforementioned range, which may explain the observed vaterite formations. However, the kinetic aspect was not considered in this simulation; this may be responsible for the discrepancy between simulated and experimental results. Currently, databases of reaction kinetics are not sufficient to allow calculation of vaterite precipitation in detail. However, the results show that it is feasible to use the geochemical model to evaluate the MC process with correction factors, since the deviation between experimental and simulated results remained fairly constant throughout the cycle.



(a) pH of solution after each process



(b) Molar concentration of calcium after each process

Figure 5-7. Comparison of simulated and experimental data for pH and amount of calcium.

Chapter 6 Conclusions

Global warming caused by rapid atmospheric accumulation of carbon dioxide is considered to be a serious issue. This study investigated the use of MC, which is the most realistic domestic option for carbon dioxide sequestration. However, MC has the drawback of excessive processing cost compared to other carbon storage options. To overcome this limitation, indirect carbonation experiments were conducted to study the possibility of producing relatively pure calcium carbonates from alkaline industrial wastes.

Ammonium chloride is known to be the most promising from among various extractants, given the potential it affords for reagent recovery and reuse. However, there is no actual test to determine whether it can be reused. In this study, additional tests were conducted in a cyclical manner to evaluate the recyclability of the NH_4Cl solution. The results obtained in this study are summarized below.

(1) Selection of appropriate industrial waste

Korea generates large quantities of several potentially suitable industrial wastes, including: approximately 15 million tons of steel slag, and approximately 120,000 tons per day of waste concrete (2012). Given this,

9,600 tons per day of waste cement were used to produce 80 kg of powdery waste cement from every ton of waste concrete. The raw slag needed pulverization with a jaw crusher and a stainless steel mill, to produce fine slag; the cement, however, was already in the form of a fine residue after recovery of aggregates by crushing demolition concrete waste and size separation. Since these material contains approximately 40 wt% Ca (as CaO), they have great potential for CO₂ sequestration.

(2) Alkaline wastes reacted with various acids

Extraction experiments were conducted with waste cement and blast furnace slag to compare extraction characteristics using hydrochloric acid, acetic acid, oxalic acid, citric acid, EDTA, and ammonium chloride as extraction agents. In all cases, the initial reaction was rapid and stabilized after several minutes. In the case of every type of acid, extraction was more effective with waste cement than with slag, when considering the maximum amounts of calcium ions in solution (2400 mg/L vs. 1800 mg/L), calcium concentration (99% vs. less than 90%), and equilibrium pH (10–12 vs. 5–8). Slag contains many potentially hazardous heavy metals that would be leached out, resulting in low calcium concentrations during extraction. This could complicate the process and the resulting carbonated products may not

be of sufficient purity to be of value in other applications, such as in the paper industry. Moreover, post-extraction residues can be environmentally hazardous and might require additional treatment. As a result, waste cement was considered to be the most appropriate material for carbonation.

(3) Production of calcium carbonate from industrial wastes

Calcium-rich solutions from each type of waste were reacted with 99.9% CO₂ to precipitate calcium carbonation. Extraction solutions of 0.1 M CH₃COOH and 0.1wt% EDTA were selected as the most effective for both blast furnace slag and waste cement. It was necessary to adjust pH by adding NaOH in order to induce effective carbonation. As the pH was increased by addition of NaOH, the extent of carbonation calculated from reduction in the calcium concentration (in both wastes) became 50% at pH 10 (a change from 95% at pH 12). The solid product obtained from waste cement was white, with particles of uniform size (under 3 μm); this was very pure calcite. The product from slag presented light brown, heterogeneous particles (mainly silicates and aluminates), which lowered its value. Waste cement was therefore evaluated as the most appropriate material to produce relatively pure calcium carbonate.

(4) Extraction efficiencies of acids with waste cement

In order to compare the extraction efficiencies of acids, waste cement was reacted while varying the concentration of three acids (hydrochloric, acetic acids, and ammonium chloride). There was little variation in the maximum amounts of calcium ions in solution when extracted using the various acids at 0.1 M. There seems to be a linear relationship between acid concentration and the maximum extraction rates of calcium in the extraction solution, regardless of acid type. However, the rate of increment depended on the type of acid. When acid concentrations were increased to 0.5 M, calcium concentrations of HCl and CH₃COOH solutions increased more than five-fold, while those of NH₄Cl increased three-fold. If all the calcium in the extraction solution was reacted with carbon dioxide, NH₄Cl could take up, up to 0.1 kg CO₂/kg cement, while HCl and CH₃COOH could adsorb 0.2 kg CO₂/kg cement.

(5) Production of calcium carbonate from waste cement

After extraction, the filtrate was reacted with 99.9% CO₂. Unlike in the case of other acids, carbonation with the extraction solution NH₄Cl was achieved without requiring the addition of basic reagents. NH₄Cl may therefore be more economical, although the solution extracted with NH₄Cl

had lower Ca content than in the case of those obtained with HCl or CH₃COOH. Consequentially, NH₄Cl can actually take up 0.07 kg CO₂/kg cement, whereas HCl and CH₃COOH can absorb 0.19 kg CO₂/kg cement. Although the maximum CO₂ mineral sequestration capacity of ammonium chloride was lower than that of hydrochloric and acetic acids, it was reasonable when compared with HCl or CH₃COOH.

After completion of the carbonation stage, additional tests were performed in a cyclical manner to evaluate the reusability of the recovered NH₄Cl solution. Calcium ions continued to accumulate in the recovered NH₄Cl solution as the conversion efficiency decreased while the number of cycles rose. NH₄OH was used to remove residual calcium ions at some point during recycling. When waste cement was dissolved via ammonium chloride extraction, flower-like particles of vaterite were precipitated. Since vaterite has higher commercial value than calcite, NH₄Cl extraction has a potential commercial advantage over other forms of acid extraction.

(6) Carbonation with flue gas

Direct carbonation was carried out using synthetic flue gases with NH₄Cl with the aim of reducing CCS cost. When reacting with N₂ and CO₂ mixtures, the pH of the solution decreased more slowly with time and it took

longer to reach equilibrium. Carbonation was unaffected by the introduction of small amounts of SO_x and NO_x to the synthetic gas. As a result, the ammonia from NH_4Cl served to separate the carbon dioxide from the gas mixture in carbonation. It was anticipated that NH_4Cl solutions would simultaneously capture and sequester carbon dioxide from real flue gas.

(7) Thermodynamic analysis

PHREEQC (a geochemical program) was used to analyze extraction efficiencies of three acids (hydrochloric acid, acetic acid and ammonium chloride) with waste cement and MC processes using NH_4Cl solution in a cyclic fashion. For the simulation, the composition of the sample was first estimated and normalized with XRD and TGA.

Initial pH of these weak acids was higher than that of hydrochloric acid at the same concentration, indicating that not all acid was dissociated into the solution. After reacting with waste cement, equilibrium pH showed a similar value across all acids, unlike initial pH. Hydrochloric and acetic acids, in particular, had the same value from 11.09 (0.1 M) to 8.19 (0.5 M). Although the types of negative ions and the amount of H^+ were different in these acids, waste cement had high reactivity to generate large amounts of Ca^{2+} at low acid concentrations. The amounts of Ca in various acid

concentrations (after reacting with the cement) were smaller than in case of experimental results. The variation became larger as acid concentration increased. However, similar to the trend for pH, hydrochloric and acetic acids had the same amount across all concentrations. After extraction, these solutions were rich in Ca, S, Al, and Si, regardless of the acid type. Calcium was present at about 93%, which was almost all in the form of Ca^{2+} form, with some in the form of CaOH^+ . S was mainly present as SO_4^{2-} and CaSO_4 , Al present as $\text{Al}(\text{OH})_4$ and $\text{Al}(\text{OH})_3$, and Si was present as H_3SiO_4^- and H_4SiO_4 . The main species of all elements were the same as in the Eh-pH diagram.

During the first stage of extraction, not all calcium was extracted from the waste cement particles. After the first stage of carbonation, the simulation estimated 95% calcium removal from solution, but only 70% removal was achieved experimentally. During subsequent stages of extraction and precipitation, the simulation indicated that the amount of Ca in solution would fluctuate within a range of fixed values in a periodic fashion. In contrast, experimental results showed accumulation of calcium following the precipitation step in each cycle. One reason for this phenomenon is that the kinetic/thermodynamic balance is controlled by the amount of Ca^{2+} and CO_2 present in the solution. The other reason is a lack of

thermodynamic data on the formation of different calcium carbonate polymorphs, which requires future study.

6.1. Concluding remarks

In this study, the potential for producing relatively pure calcium carbonates from blast furnace slag and waste cement was assessed for the first time. The findings show that the carbonation of slag would produce lower grade calcium carbonate and that it is too expensive as a CO₂ storage process due to the need for pulverizing. However, it was also found that relatively pure calcite could be synthesized by carbonating cements under ambient conditions without any pre-treatment. Another structure of calcium carbonate (vaterite) could be also produced by using ammonium chloride used as an extraction agent; this is expected to be able to increase the utilization value of by-products. When comparing these results, waste cement appears to be a more appropriate material for MC.

Ammonium chloride is known to be the most promising reagent, given the potential for reagent recovery and reuse. However, there is no actual test to determine whether this can be reused. Actual experiments were conducted in a cyclical manner to evaluate the recyclability of the NH₄Cl solution.

In addition, a PHREEQC simulation was conducted to help understanding of the optimum reaction, which was found to be useful for predicting reactions under other conditions.

Reliable experimental data would be valuable for further development of a functional MC process. This work presents experimental data with respect to the extraction of industrial wastes using various acids. The results give an overview of the suitability of common solvents (HCl, CH₃COOH and NH₄Cl) for the extraction of calcium. Apart from their application in MC processes for the storage of CO₂, the results can also be used in the mineral processing industry, where valuable metals are extracted from wastes.

6.2. Future Research

Although waste cement and ammonium chloride were shown to be preferable materials for carbonation, all experiments in this study were conducted at laboratory scale. An important next step in aqueous MC research is a pilot-scale study of the carbonation reaction under continuous conditions and at a larger scale. Further insights into carbonation mechanisms can therefore be obtained by studying extraction and

carbonation mechanisms at elevated temperature and pressure, which may help to provide more results concerning technical feasibility.

Research on the re-use possibilities of carbonation products is recommended, particularly with regard to determination of value and volume of possible markets. The beneficial utilization of these products can contribute to a substantial reduction of sequestration costs. In fact, MC will be more effective if the product can be usefully applied. Comprehensive and accurate analysis of energy consumption and sequestration costs, including CO₂ capture, mining, and transportation process steps, also be included for application at industrial scale.

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Abstract

Comparison of Various Extractants for Mineral Carbonation of Industrial Wastes

문명옥
에너지시스템공학부
서울대학교 대학원

요약 (국문 초록)

광물탄산화는 국내 여건 상 가장 현실적인 기술 중 하나로 평가 받고 있다. 탄산화 반응속도를 높이기 위한 다양한 연구가 진행되고 있지만, 광물 탄산화는 여전히 연구단계에 머물러 있다.

탄산화 효율을 평가하기 위해 고로슬래그와 폐시멘트를 상온, 상압 조건에서 동일 농도 (0.1M)의 다양한 산과 반응시켰다. 용출제로는 염산, 아세트산, 옥살산, 시트르산, EDTA, 염화암모늄이 이용되었다. 폐시멘트가 EDTA 를 비롯해 다양한 산과의 반응에서 용출되는 최대 칼슘 양 (2400 mg/L)과 순도 (99%)가 슬래그보다 높게 나타났다. 이것은 시멘트가 다공질 구조로 슬래그보다 비표면적이 넓어 반응성이 높기 때문이다. EDTA 첨가 시, 용출효과는 증대시켰으나 탄산화 반응에 염기의 사용량을 줄여주는 효과는 기대할

수 없었다. 유기산 (옥살산, 시트르산)은 칼슘용출에 영향이 거의 없었다. 각 산업부산물에서 용출반응 이후, 칼슘이 풍부한 용액과 99.9% 이상의 순수한 이산화탄소와의 반응을 통해 탄산칼슘을 침전시켰다. 폐시멘트로부터 용출된 칼슘이 풍부한 용액을 탄산화 반응을 수행한 결과, 높은 순도의 탄산칼슘을 침전시킬 수 있었다. 그러나, 슬래그로부터 용출된 용액은 규산염과 알루미늄산염의 존재로 인해 다소 순도가 낮은 탄산칼슘이 생성되었다.

위의 결과를 통해 폐시멘트를 광물탄산화에 적합한 시료로 선정하였고, 염산, 아세트산, 염화암모늄을 용출제로 실험을 수행하였다. 산 농도가 낮은 조건 (0.1M)에서, 용출된 칼슘의 양은 산 종류에 관계없이 유사했다. 산 농도가 0.5M로 증가함에 따라 용출량은 선형관계로 일정하게 증가하였으나, 증가율은 산 종류에 따라 다르게 나타났다. 염화암모늄이 염산과 아세트산에 용출된 칼슘의 양은 적었으나, 탄산화 반응에서 염기성물질의 투입 없이 바테라이트형 탄산칼슘이 생성되었다. 또한, 염화암모늄은 탄산화 과정에서 다시 생성되어 칼슘용출에 재사용할 수 있었다. 그러나, 칼슘이온이 이산화탄소와의 반응을 통해 탄산칼슘으로 완전히 전환되지 않아 지속적인 누적되는 현상이 발생했다. 완전한 재활용을 위해서는 탄산화 반응에서 추가공정이 필요하겠지만, 이런 염화암모늄의 특성은 다른 산에 비해 매우 경제적인 용출제임을 나타냈다. 추가적으로, 배기가스와의 직접적인 탄산화 반응을 수행하여 이산화탄소 포집에 소요되는 비용을 줄여 보다 효율적인 광물탄산화법을 제시하였다.

가장 효율적인 산업부산물과 용출제인 페시멘트와 염화암모늄의 반응을 지구화학적 반응 모사 프로그램인 PHREEQC 를 이용하여 실험에서 도출된 결과와 비교하였다. 이 프로그램에서의 반응은 열역학적 평형을 기반으로 계산되었다. 반응 분석결과, 초기 pH 는 해리상수로 인해 아세트산이 염산보다 높았지만, 시멘트와 반응 후의 pH 와 용액에 존재하는 칼슘이온의 양은 유사하였다. 이 결과는 실험에서 도출된 결과와 동일한 경향을 나타냈다. 각 이온의 복합염 생성여부를 확인하기 위해 모델링을 통해 존재형태를 분석하였다. 용액 내의 칼슘이온 주로 Ca^{2+} 와 CaOH^+ 로, S 는 SO_4^{2-} 와 CaSO_4 , Al 은 $\text{Al}(\text{OH})_4^-$ 와 $\text{Al}(\text{OH})_3$ 로, 그리고 Si 는 H_3SiO_4^- 와 H_4SiO_4 로 존재하는 것을 확인하였다. 이 결과는 Eh-pH 그래프와 동일했다. 염화암모늄을 재사용하는 과정에서 용출된 칼슘의 양은 일정하여, 실제 실험에서 칼슘이 누적되는 현상과 차이가 있었다. 이런 현상은 용액 속에 존재하는 Ca^{2+} 과 CO_2 의 양에 따라 열역학적 균형이 조절되기 때문인 것이다. 그러나 프로그램 결과와 실험 결과와 일정한 차이를 보여, 보정계수를 적용한다면 광물탄산화법을 분석하는데 유용할 것이다.

주요어: 광물탄산화, 페시멘트, 고로슬래그, 염화암모늄, 열역학적 모델링

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