CARBON DIOXIDE UTILIZATION THROUGH INTEGRATION OF SHALE GAS

PROCESSING AND INDUSTRIAL WASTE MINERALIZATION

A Thesis

by

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ABSTRACT

As anthropomorphic levels of carbon dioxide continue to rise, it is necessary to implement responsible production practices to minimize the greenhouse gas created in industrial processes. One such process of interest is that of shale gas, which is expected to increase in production and become our dominant natural gas source within the next few decades. Currently, carbon dioxide sequestration techniques like enhanced oil recovery (EOR) and geological sequestration have helped alleviate some of the burden. However, these methods only serve to store limited amounts of CO2 and do not reduce the overall global net levels.

In this study, the utilization method of mineralization is investigated as a potential integrated process to turn CO2 into value added products. Furthermore, the use of industrial waste as a mineral feedstock is implemented to facilitate sustainability practices. Through Aspen modeling and simulation, the integrated process can be evaluated for several waste sources and the overall economics can be analyzed to determine financial viability.

Results indicate that over a large range of waste compositions the process could return a considerable profit over a relatively short time span. Cost sensitivity analysis also demonstrated the systems flexibility for fluctuations in product price points. The results of this study will hopefully encourage further look into CO2 utilization methods as not only an environmentally oriented practice, but as a profitable and sustainable option.

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NOMENCLATURE

EOR	Enhanced Oil Recovery
CO_2	Carbon Dioxide
GHG	Greenhouse Gases
CCS	Carbon Capture and Sequestration
CCU	Carbon Dioxide Utilization
EGR	Enhanced Gas Recovery
μm	Microns
ΔH_{rxn}	Heat of Reaction
MWSI	Municipal Solid Waste Incineration
CKD	Cement Kiln Dust
Mt	Million Tons
EGP	Economic Gross Potential
MISR	Metric for Inspecting Sales and Reactants
PCC	Precipitated Calcium Carbonate
USD	U.S. Dollars
°C	Celsius
MMscfd	Million Standard Cubic Feet per Day
hr	Hour
wt%	Weight Percent
kW	Kilowatts

MWh	Megawatt-hour
FCI	Fixed Capital Cost
WCI	Working Capital Investment
TCI	Total Capital Investment
ROI	Return on Investment
AFC	Annual Fixed Costs
AOC	Annual Operating Costs

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

It is no surprise that there is a growing concern over atmospheric conditions and how greenhouse gasses are (GHGs) affecting our environment. Carbon dioxide (CO_2) is one of the main components of growing GHG levels and accounts for nearly 77% of industrial GHG emissions.[1] In order to begin the process of restoring atmospheric GHG levels to acceptable conditions, sustainable practices should be implemented in order to reduce and minimize emissions created through industrial processes. This is easier said than done obviously, as GHGs like CO_2 are typically considered as waste with no inherent chemical value due to their low-energy nature. Luckily, attention has been focused on finding ways of capturing, storing, or utilizing CO_2 in meaningful ways to help mitigate emissions and turn CO_2 into a useful commodity.

Utilization vs. Sequestration

Generally speaking, CO_2 uses can be separated into two categories: sequestration and utilization. Carbon capture and sequestration (CCS) is the method of capturing carbon dioxide from sources like emissions or even the atmosphere in order to separate and store the gas in an environmentally beneficial manner. One of the most popular forms of CCS currently is that of enhanced oil recovery (EOR). With this method, CO_2 is injected at well sites in order to increase pressure and flush out oil that may have remained after initial pumping. Typically, at a new drill site, only about 20-40% of the oil is initially obtained. EOR can help recovery around 5-30% of oil that would otherwise be missed.[2] Afterwards, the CO_2 can be geologically sealed off in the well to prevent its escape back into the atmosphere. While this makes good use of CO_2, this does

1

not affect its net levels or help to reduce its presence. There is some uncertainty towards using EOR or other geological sequestration techniques as a long-term solution due to the possibility of leaks and the need for constant monitoring of the sites.[3] Along with this, there is an issue of public acceptance with storing CO_2 underground.

Carbon dioxide utilization (CCU) can circumvent these issues in that the CO_2 is chemically converted and can be considered as a more permanent "molecular" sequestration. As mentioned earlier, one of the main issues with CCU is that CO_2 is a very stable molecule and requires either highly reactive co-reagents or large energy inputs in order to convert it into anything chemically useful. However, research has shown there are several viable routes for utilization like polymer synthesis, fuel production, and biological conversion.[3] While large scale implementations of these practices are not yet common, it has been argued that they have the potential to mitigate climate change and could help lead to a low-carbon economy.[4] With proper integration and optimization, more routes for CCU could become economically viable and turn CO_2 into a useful feedstock.

Shale Gas

With the advancements in horizontal drilling and fracking techniques, the natural gas trapped inside shale formations has become much more accessible. Due to the rock's low permeability, normal drilling techniques could not adequately release the gas. Presently, shale gas is quickly becoming a dominant source of natural gas, accounting for 44% of the total natural gas production in the U.S. in 2015.[5] Similar to natural gas, shale gas consists primarily of methane along with other heavier hydrocarbons. Small fractions of the gas are also composed of CO_2, nitrogen, and sometimes even hydrogen sulfide. The exact composition of the gas varies from well to well, which may also contain other trace chemicals. Before the gas can transported

along pipelines, it must go through processing to remove impurities down to acceptable levels. One of the first steps of this process is the acid gas removal stage, where most of the CO_2 is separated. What is interesting about this stage is how pure the CO_2 stream is exiting from this acid gas removal stage. It is typical to have streams that are around 99% pure CO_2, yet most often this stream is vented directly into the atmosphere.[6] There is growing interest in using CO_2 for enhanced gas recovery (EGR), however this is nowhere near as prevalent or developed as EOR. While EGR and EOR are usually the main alternative to venting the CO_2, not much focus is present on utilizing the stream for purposes of CCU and creating value-added products.

Mineralization

Mineralization is a CCU method where CO_2 is reacted with calcium and magnesium containing minerals to produce carbonates. What is unique about this compared to other CCU processes is that the conversion of CO_2 into carbonate is thermodynamically favorable and exothermic. With this transformation into a more stable molecule, the CO_2 is permanently stored in a solid matrix. Two main routes exist for CO_2 mineralization: in-situ and ex-situ. In-situ mineralization involves injecting pressurized CO_2 underground to react with minerals and form carbonates. Ex-situ instead uses mined minerals or alkaline materials and reacts them with CO_2 in controlled conditions. While there are abundant geological minerals that are capable of mineralizing CO_2 like olivine, serpentine, and wollastonite, the in-situ method only serves as a permanent form of CO_2 storage and doesn't help to create any valuable products.[7] One of the major downsides of mineralization as a form of CCU is that the reaction is kinetically limited. In-situ mineralization is a slow process and one of the benefits of the ex-situ method is the capability to careful control and optimize the process to the point of reactions only taking hours rather than decades. However, in order to reduce reaction times there is a large penalty to pay in

3

terms of energy. One of the first steps to ex-situ mineralization is to grind down alkaline

minerals to increase surface area usually to particle sizes on the order of 10-100 μm.[7] This

process, along with high reaction temperatures, is quite energy intensive and careful

consideration must be taken to ensure this energy demand is not creating more CO_2 than it is

utilizing.

Table 1 Mineralization Properties of Common Non-Carbonated Minerals.

Mineral	Carbonation Products	Carbonation Potential (kg CO_2/kg Mineral)	ΔH_{rxn} (kJ/mol CO_2)
Olivine	$MgCO_3(s)$, $SiO_2(s)$	0.56-0.63	-89
Serpentine	$MgCO_3(s)$, $SiO_2(s)$, $H_2O(aq)$	0.40-0.53	-64
Wollastonite	$CaCO_3(s)$, $SiO_2(s)$	0.38	-90

Adapted from sources 7, 8

Additional steps may be taken to help facilitate the carbonation process. Acid dissolution

is one way of chemically preparing the minerals for easier reactivity. In a two-step process, the

dissolved mineral ions are then subjected to basic aqueous conditions where CO_2 is bubbled

through. Catalysts and chelating agents have also shown potential in further accelerating the

process. When operated under the right conditions, relatively pure products like calcium

carbonate, magnesium carbonate, and silica are some of the possible value-added materials to be

obtained. Applications for these products range from paper, plastic, and construction fillers to

glass and ceramic materials.[7]

An interesting approach to avoid some of these complications is to utilize alkaline industrial waste sources as a substitution to these natural minerals. Common wastes like fly ash and waste cement are high in calcium content and can undergo carbonation to produce calcium carbonate products. As some of these sources already exist as particulate matter, there is little to no need for comminution. More details on these waste sources are discussed in Chapter 2.

CHAPTER II

PROBLEM STATEMENT AND APPROACH

The main objective of this project is to utilize and take advantage of the high purity CO_2 stream produced from shale gas processing and integrate it with the CCU process of mineralization in order to create a sustainable and profitable system. Specifically, industrial waste will be investigated as a feedstock for mineralization due to its high carbonation potential and additional sustainability implications. Several waste sources will be considered and screened through an initial economic analysis to determine viability. Through literature analysis and reported experimental data, the integrated carbonation processes will be simulated using Aspen modeling as a method of detailed analysis. The optimized and finalized flow sheets will help evaluate mass and energy consumptions as well as estimations on equipment costs in order to fully evaluate the capital and operating costs of implementing the integrated processes. This will determine which processes are viable, profitable, and worth pursuing.

In order to get the most use out of purchased and installed equipment for the carbonation process, it would be preferential to have a system that is adaptable to a variety of waste sources without the need for individualized reaction or separation vessels. Figure 1 shows this concept of a very simple and generalized process diagram which highlights the most important units. Here, it is clear to see how the two processes of shale gas processing and waste mineralization are integrated with the connection of a carbon dioxide exchange stream. This CO_2 stream is fed into a reaction vessel along with the chosen industrial waste particles and brine solution where carbonation occurs. Next, the mixture is transferred to a separations unit where reacted carbonate

products are collected and unreacted materials and solvent are recycled back to the reaction

vessel.
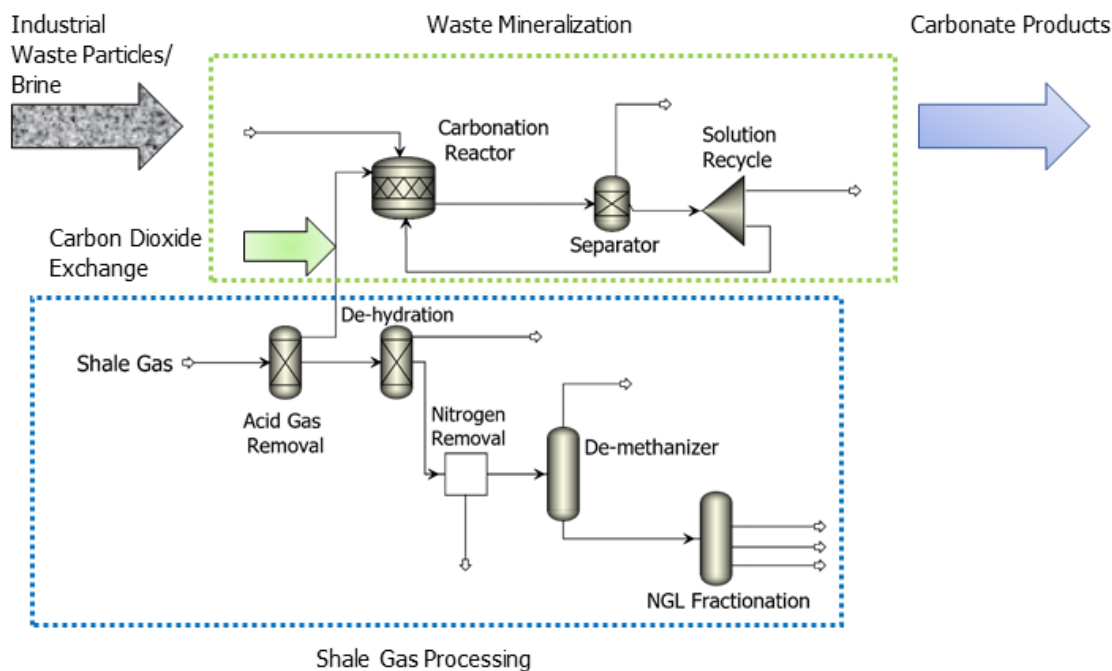
Figure 1 Generalized Flowsheet of Integrated Gas and Mineralization Processes.

Waste Source Considerations

For the purposes of this work, industrial waste sources will be considered based some of

the following characteristics: calcium content, availability, composition variability, and initial

physical properties like particle size. Obviously, the ideal waste source would have high calcium

content, small particle sizes, and would be readily available in large quantities. However,

industrial wastes vary greatly from one location to another and even within the same processing

plant. In this section, some of the more viable waste sources will be considered and discussed

Fly Ash

Fly ash is generally produced as a byproduct of coal combustion but can be produced through other combustion processes like municipal solid waste incineration (MWSI). The current production of fly ash is estimated around 500 million tones globally, with only around 16% of it being utilized in ways other than being disposed of in landfills.[9] Fly ash particles consist of toxic trace elements which can lead to environmental concerns when disposed of without treatment. While compositions vary, fly ash is broken into two classes: Class F and Class C. The main difference between the two is the calcium, silica, and iron content. Class F ash contains around 1-12% calcium while Class C contains around 30-40% calcium content. Fly ash exists as fine spherical particles, typically with sizes around 75 µm and surface areas as high as 1000 m^2/kg. As a hazardous byproduct, the cost of purchasing fly ash mostly consists of transportation costs which approximate to around $15/ton.[9] Compared to the criteria for what is considered a desirable waste source, fly ash is a highly viable option for mineralization due to its abundance and high calcium content.

Waste Cement/Cement Kiln Dust

As buildings are demolished and waste concrete is pulverized, powder byproducts are formed as aggregates are recycled. This powder is known as waste cement powder, or waste cement for short. This waste cement can make up as high as a third of total waste concrete and currently is mostly used as roadbed material or is disposed of. Waste cement averages around 30% calcium content and has a typical particle size distribution around 10-200 µm.[10] Similarly is the source of cement kiln dust (CKD), a byproduct of the cement manufacturing process. Cement manufacturing produces millions of tons of CKD annually, of which most of it is disposed of in landfills. Calcium oxide content can range from 20-60% with compositions varying depending

on where the CKD was obtained. [11] With around 15-20 tons of CKD produced for every 100 tons of cement, it is also a highly abundant waste source.[12] Both sources are also potentially hazardous, but due to their abundance and small particle sizes, it is likely mineralization could be used to viably transform them into safer, useful products.

Steelmaking Slag

Steel slag is a byproduct of the steel manufacturing process. Initially a molten liquid, steel slag cools into a mixture of oxide and silicate materials. This can refer to multiple steps of the process and the waste may have corresponding names like furnace slag or ladle slag. Typically, steelmaking slag contains around 25-55 wt% calcium oxide and has been proven to effectively produce calcium carbonate at relatively low pressures and moderate temperatures with proper solution conditions.[13] Steelmaking slag is produced globally at about 200 Mt annually and typically is formed at a ratio of 0.2 tons of slag for every ton of steel.[14] Size distributions greatly vary from source to source with ranges on the order of 1 mm-1 cm and may require further comminution.[15] As with the other sources, efficient CO_2 utilization will depend on the characteristics of the slag undergoing carbonation, but present work has shown promising results for a variety of steelmaking slag compositions and reaction conditions.

Other Wastes

While the waste sources above are the most prevalent, there are a vast amount of other alkaline industrial waste sources, like red mud and other process waste. While these sources may also have high alkalinity and small particle sizes, the main limitation will be the availability for industrial scale operations.

Brine Water as a Solution

Saline wastewater is a common byproduct during the production process of oil and gas. About 20-30 billion barrels of this wastewater is produced annually in the US, where around 65% is reinjected into well sites as a means of pressure control.[16] The remaining wastewater is typically either treated or discharged. Discharging saline water into the environment has obvious negative implications and treatment costs can range anywhere from a few cents to a few dollars per barrel. Part of this discrepancy is due to differences in local regulation standards, but another reason stems from the fact that brine has varying concentration of Ca, Mg, and Fe along with the standard Na and Cl ions. While adjustments need to be made to the brine water, its utilization as a medium for mineral carbonation could lead to a higher productivity due to the presence of these ions, specifically calcium.

Carbonate formation occurs under pH conditions of 7.8 or higher. Because the typical pH range of brine is about 3 to 5, it needs modification before carbonation can happen. The addition of the industrial waste material will help to increase the pH of the brine and can reach reaction conditions with enough waste. However, the pH can be more readily adjusted with the addition of bases like NaOH. While additional reaction reagents like NaOH could help to decrease process time, its environmental and economic impacts need to be carefully considered. Existing research is limited on what conditions are optimal for carbonation in brine (pressure, temperature, etc.) but simulation optimization will hopefully help to supplement these missing parameters.

Initial Analysis

It would be an inefficient use of time if every consideration for a waste source feedstock was simulated in order to determine if the choice is economically feasible or not. Luckily,

screening methods exist that provide a rough but quick analysis as to whether or not a process

may be profitable. For these methods, the only necessary information is the purchase price of

feedstock, the selling price of products, and the stoichiometric relationships between the

materials. One such method is the Economic Gross Potential (EPG), which in simple terms

checks that the rate of profit from products is higher than the rate of purchasing feed. In the next

sections, a very similar method will be used to evaluate some of the waste sources listed

previously.

MISR Definition

The Metric for Inspecting Sales and Reactants (MISR) is a ratio of product sales to

reactant purchases. Any process that has an MISR greater than 1 has a chance of being

profitable, while any value lower than 1 indicates the process is not economically feasible. The

MISR equation is defined below as:

$$MISR = \frac{\sum_{P=1}^{N\ products} Annual\ Production\ Rate\ of\ P * Selling\ Price\ of\ P}{\sum_{R=1}^{N\ reactants} Annual\ Feed\ Rate\ of\ R * Purchase\ Price\ of\ R}$$

It should be noted that an MISR value greater than 1 does not guarantee a profitable

process, as a full detailed analysis is necessary to determine profitability. However, a value

greater than 1 does justify further investigation into the process. This method helps quickly weed

out any processes that have no chance of viability rather than wasting effort on unnecessary

analysis.

Waste Evaluation

In order to perform an MISR analysis on previously mentioned waste materials, the purchasing prices and product selling prices must be realistically set first. This data was gathered through literature and will be used for this analysis. The more difficult aspect of the MISR evaluation is determining the stoichiometric relationship between the waste and the carbonate products due to the variation in composition. For the purposes of this analysis, it will be assumed that the wastes consist of 30 wt% calcium oxide, as this falls within the range of each of the considered waste sources. The CO_2 feed is obtained from the shale gas process, and brine is considered to be present within the existing infrastructure and therefore assumed to also be available as feed. The primary target product for this study will be precipitated calcium carbonate (PCC), a high purity material used in ceramics, fillers, and other chemical applications. While ultrahigh purity calcium carbonate can reach market prices of USD 10,000 per metric ton, a more realistic quality (~98%) will be considered here with a typical market price around USD 400 per metric ton.[10] With these set parameters, a stoichiometric ratio of 1.87 kg waste/kg PCC is established assuming all reactant material is converted.

Table 2 MISR Evaluations of Waste Carbonation.

Waste Material	Approximate Price (USD/metric ton)	MISR
Fly Ash	15 [9]	14.3
Cement Kiln Dust	17 [17]	12.6
Furnace Slag	13 [18]	16.5

As indicated by the MISR values in Table 2, the waste carbonation reaction appears to be potentially profitable. Of course, this evaluation does not consider utility costs or other potential reactants, but this is saved for further analysis.

The Two-Step Approach

Two main strategies exist for mineralizing waste particles: The single-step approach and the two-step approach. A single step approach involves mixing waste particles in an aqueous solution where CO_2 is then also bubbled through in the same reactor. The two-step approach separates these processes, where the calcium ions are first leached into solution and the remaining solid waste is filtered out so CO_2 can be mixed to form pure calcium carbonate without other solids affecting purity. While the single-step approach is much more direct and easier to implement, the two-step approach will produce the purified product of interest and is more economically favorable in this case. The two-step approach also allows further process control and tuning. Leaching calcium ions out of solid particle waste is favored at lower pH ranges while carbonation only occurs in more basic conditions. These competing reaction conditions make it difficult to be efficient in the single-step approach without the use of complicated pH swing techniques.[7] All simulated processes in this research will implement the two-step approach in order to increase efficiency of producing high purity PCC.
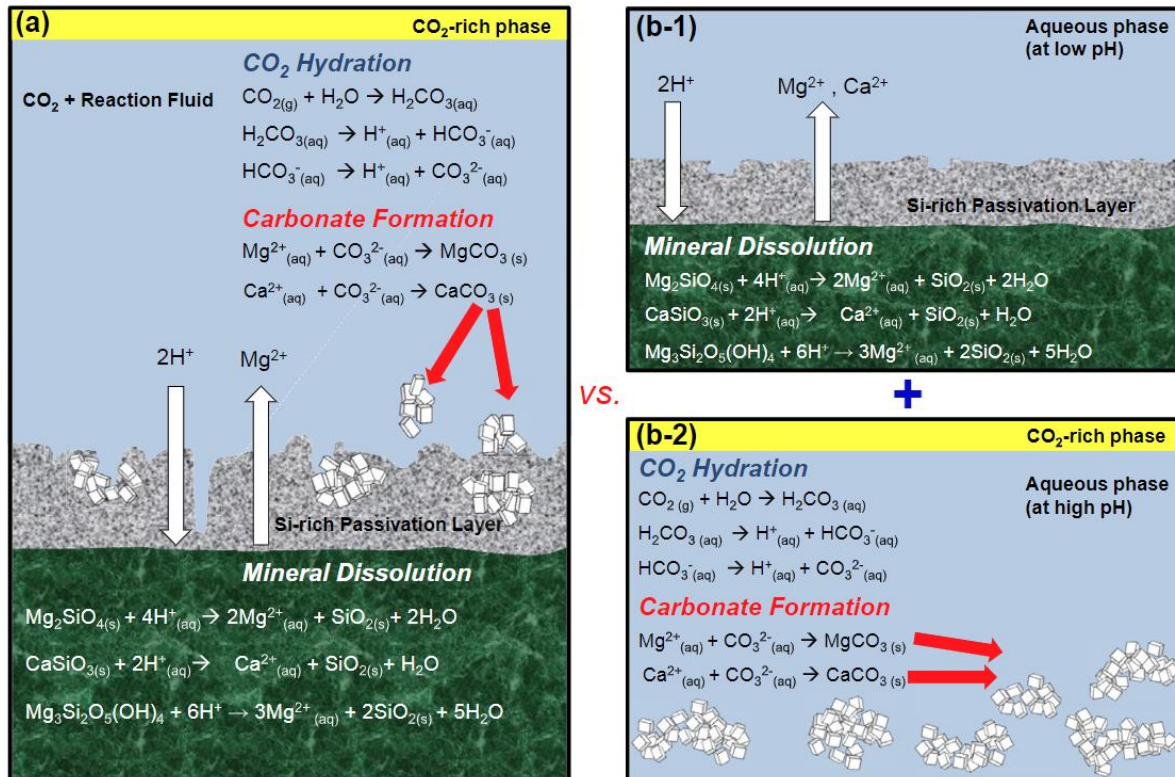
Figure 2 Single-step and Two-step Approach Schemes (Reprinted with permission from *Carbon Dioxide Utilisation***, by Greeshma Gadikota, Ah-hyung Alissa Park, 2015, Elsevier Books. Copyright [2019] by Elsevier)[7]**

CHAPTER III

REACTION MODELING

Other than the weight percent of calcium content, the major difference between the three types of industrial waste being considered in this project is the form in which the calcium is stored. These waste particles contain various types of silicates, ores, metals, and hydrates which influence the effects and composition of the leaching solution. In order to account for these differences, the proper chemical systems of each waste type need to be considered to describe the processes. Before these systems are described, there are a few simplifications that can be made. First, it has been noted that with these types of industrial wastes, calcium, hydroxide, and sulfate ions are the main leachable components, followed by potassium and minor levels of sodium, aluminum, and magnesium. The sum of the three main leachable ions typically account for 90-95% of the electroneutrality condition.[19] With this information, we can drastically reduce the amount of chemical equilibriums that need to be incorporated in the simulation and focus on the major components. While it has been stated that the dissociation of calcium sulfide (CaS) is also present, this can be neglected at lower mass fractions ($<0.1wt\%$)[20]. Other than these leachable components, the rest of the waste can be assumed as an inert solid which will be filtered out following the leaching stage.

Leaching Waste Cement

Waste cement is typically composed of SiO_2, CaO, Al_2O_3, MgO, and Fe_2O_3.[21] From this, we can infer that the free lime (CaO) component will be the main calcium source. When free lime is mixed within an aqueous solution, calcium hydroxide ($Ca(OH)_2$) is formed. This is a somewhat soluble precipitate which will dissociate a hydroxide group first, followed by the

15

remaining hydroxide and calcium ions in a second equilibrium step. The equilibrium descriptions are stated below.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 \rightarrow CaOH^+ + OH^-$$

$$CaOH^+ \rightarrow Ca^{2+} + OH^-$$
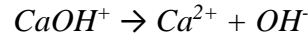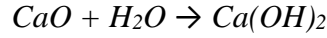
While the first step can be assumed to react to completion, the following two dissociations require equilibrium data to determine the resulting concentrations. Both equilibrium constants were found through literature and were input into Aspen to help model the system.[22]

Leaching Fly Ash

Fly ash can contain a great variety of materials in varying amounts, however the main components are typically SiO_2, CaO, Al_2O_3, MgO, K_2O, $CaSO_4$ and Fe_2O_3.[16] While similar to the components found in waste cement, one key difference is the presence of calcium sulfate which represents another viable calcium source. In the presence of water, calcium sulfate forms a hydrated complex known as gypsum. This solid hydrate is slightly soluble and dissociates to form calcium and sulfate ions along with the complexed water. While the free lime component can be assumed to follow the same equilibrium conditions as the waste cement, this gypsum component is described by the equations below.

$$CaSO_4 + 2H_2O \rightarrow CaSO_4 \bullet 2H_2O$$

$$CaSO_4 \bullet 2H_2O \rightarrow Ca^{2+} + SO4^{2-} + 2H2O$$
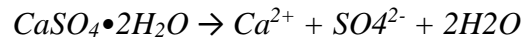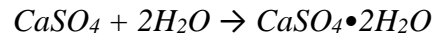
The parameters for these equilibrium states are present in Aspen and were utilized in the simulation.
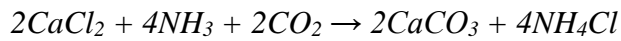
16

Leaching Steelmaking Slag

Steelmaking slag contains a complex mixture of silicates, srebrodolskite, and calcium/magnesium-wustite type phases.[23] While free lime is present in small amounts, it typically is bound within the wustite phases and cannot react in the leaching process. In this case, the main leachable calcium content comes in the form of dicalcium silicate (Ca_2SiO_4). For this project, the dissociation equation will be assumed as stated below.

$$Ca_2SiO_4 \rightarrow 2Ca^{2+} + SiO_4^{4-}$$

The calcium in this phase is more difficult to extract than the calcium present in the previous waste types. While acids can improve extraction efficiency, the impose greater environmental concerns as well as a higher operating cost. An interesting solution that will be implemented in this project is the use of ammonium salts as described in the next section.

Ammonium Salts

As mentioned in the section on the two-step approach, the leaching process favors acidic conditions while the carbonation stage requires basic conditions. Using acid to improve extraction efficiencies would cause difficulties and the possible necessity of additional basic material to make the carbonation process possible. One suggestion is the addition of ammonium salts like NH_4Cl which, while less effective at leaching than acids, still manage to improve efficiencies without drastically impacting the pH level. In addition to this, the ammonium salts are regenerated after the carbonation step which helps to improve process economics.[21] The following reaction equations show an example of how the salts interact in the leaching and carbonation stages.

$$2CaO.SiO_2 + 4NH_4Cl \rightarrow 2\ CaCl_2 + 4NH_3 + 2H_2O + SiO_2$$

$$2CaCl_2 + 4NH_3 + 2CO_2 \rightarrow 2CaCO_3 + 4NH_4Cl$$

Different ammonium salts have different impacts on both the extraction efficiencies as well as the carbonation efficiencies of varying waste types. A high extraction efficiency doesn't correlate to a good carbonation efficiency. Additionally, the efficiency of some salts may vary greatly with concentration while others aren't impacted as heavily. For example, in the study of ammonium salt effects on waste cement leaching, NH_4NO_3 varied from an efficiency of 68.8% at 1M to an efficiency of 60.1% at 0.5M, while the salt CH_3COONH_4 varied from 69% at 1M to 23.8% at 0.5M.[21]

Carbonation of Leached Calcium

While the extraction mechanisms differ between the waste types, the carbonation process is virtually the same between them all since it is only the leached calcium ions taking part in the reaction and none of the other ions. Because of this, the reactor can be modeled using the same set of equilibrium equations across all three waste types. In this reactor, CO_2 is bubbled through the solution to first produce bicarbonate, which in turn reacts to form the carbonate species. This carbonate ion reacts with the leached calcium ions to precipitate as the target calcium carbonate. The simplified set of equations is shown below.

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$
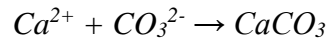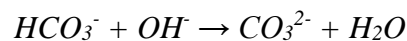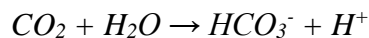
As an example, literature has shown that with the process of leaching and carbonation of ash waste, a precipitated calcium carbonate product of ~99% purity is obtained.[20]

Defined Project Efficiencies

While it is possible to simulate these systems in Aspen utilizing kinetic and equilibrium data, the results are not always accurate. Instead, this project will utilize present experimental

data from literature to define reaction efficiencies. While this may limit the operating conditions to those defined in the literature, the resulting computational model should produce a more realistic simulation. With everything considered so far, the following three waste source scenarios will be explored along with the determined efficiencies:

1. Fly ash (no ammonium salts)- extraction efficiency will be determined by Gibbs reactor; Carbonation efficiency is approximately 87%.[20]

2. Waste Cement with NH_4NO_3 salt- extraction efficiency of 60% at salt concentration of 0.5 M; Carbonation efficiency is approximately 74%.[21]

3. Steelmaking Slag with NH_4Cl salt- extraction efficiency of 35% at salt concentration of 2.0 M; Carbonation efficiency is approximately 84%.[21]

All data was produced at ambient condition (25℃, 1 bar) and will be reflected as such in simulation parameters.

CHAPTER IV

SIMULATION DESIGN

Three separate flowsheets were created for each of the waste sources being analyzed. While the feed streams and compositions may vary between them, the units and connections between them are the same in order to maximize the flexibility of the system when switching between types of industrial waste. An example of the process design can be seen in Figure 3. First, the raw industrial waste is processes through a crushing unit in order to get the particles down to the designated size distribution. The refined waste is then sent to the leacher where it is mixed with water, brine, extraction salt if applicable to the system, and an aqueous recycle stream. After the particles have been leached of the calcium ions, the solution is sent through a filter to remove any remaining solid particles as detailed by the two-step approach. The filtered solution is then passed into the carbonation reactor where CO_2 is bubbled in to be mineralized with the alkaline solution. The stream, now present with precipitated carbonate material, is then passed through another filter represented as a separator to remove the PCC product. Finally, the remaining electrolytic solution is sent to a splitter in order to recycle a specified fraction.

The scale for this project will be based on a case scenario of a 100 MMscfd shale gas processing plant. This equates to an approximate feed flow of 94200 kg/hr worth of shale gas. The mass composition of CO_2 in shale gas varies from well to well, usually in the range of 1 to 9 wt%. Taking a median value of 5 wt% CO_2 and assuming the acid gas removal process produces a pure CO_2 stream, this equates to a flow rate of about 4700 kg/hr. Based on this reasoning, the flowsheets in the project will utilize a 5000 kg/hr feed of CO_2.
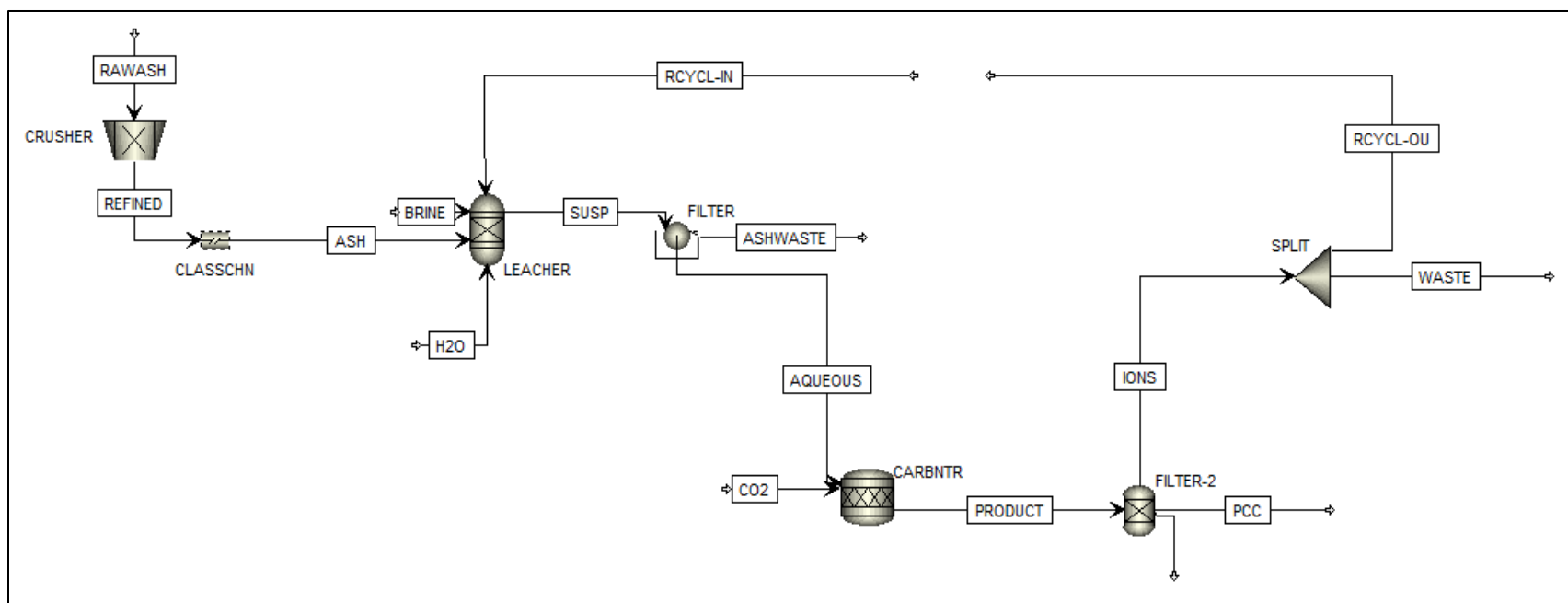
Figure 3 General Process Flow Diagram.

Set-Up Considerations

In order to accurately simulate the intended processes, the chemistry needs to be properly defined in the program. The ELECNRTL property method was used in Aspen in order to describe the highly electrolytic solutions being modeled and to account for the numerous dissociation and precipitation reaction equilibriums. While some equilibrium data is available in Aspen for the present species, missing parameters must be filled in with external data. The process can be divided into two major reaction components: the leaching unit and the carbonation unit. Because the leaching unit only contains sets of dissociating and equilibrating species, a GIBBS reactor block was used to model this process. The carbonator however is the specified unit for containing the mineralization reaction and is modeled using a STOICH reactor block. Details on these two units are listed in the sections below.

The Leacher

The GIBBS reactor block in Aspen takes the defined chemistry, thermodynamic, and equilibrium data to minimize the Gibbs free energy of the mixture input to caclulate the thermodynamic equilibrium. Data from literature indicates that for leaching systems using waste particles of sizes smaller than 150 microns steady-state is reached in well under two hours.[23] This steady-state system can be approximated as an equilibrium and justifies the use of a GIBBS reactor unit. The specific components present in the reactor depends on the waste being utilized.

As specified in the defined efficiencies section, flow sheets involving the use of ammonium salts will utilize the extraction efficiencies reported in literature as a

constraint in the Gibbs equilibrium calculations. This is done by placing restricted

equilibrium definitions in the unit description parameters. By modifying the molar extent

of the specific calcium leaching reaction in question, the proper extraction efficiency can

be replicated and the remaining components in the system can reach equilibrium based

on this constraint.

The Carbonation Vessel

The two input streams to this unit are the pure CO_2 coming from the theoretical

shale gas plant and the filtered aqueous stream containing the leached ions. Because we

are considering the calcium to be the only reacting component from this aqueous stream

and have available carbonation efficiency data, we can model this reaction vessel using a

STOICH reaction block. Here, the defined carbonation reaction mechanisms as mention

in the previous chapter can be defined and restrained with a fractional conversion of

calcium equivalent to the efficiency data.

The Crusher

The first unit in the process design is the crusher where unrefined ash is

pulverized down to a predetermined size and fed into the leaching unit. While the cited

literature typically uses particle sizes in the region less than 150 microns, for this project

particles will be comminuted down to a distribution around 75 microns in order to assure

proper equilibrium is reached in the leaching unit. Indeed, it was determined that

between variations of particle size, vessel temperatures, and leaching times, the size

distribution of the waste particles had the largest impact on how quickly the system

reached steady-state.[23]

The utility of the crushing unit is a function of the particle size distribution being input into the system. In order to evaluate and take into consideration the varying possible particle sizes of imported wastes, a sensitivity analysis will be performed to determine the utility usage across a range of plausible waste sizes.

Filters and Recycle

Two filters are implemented in the process design, one after the leaching unit and another after the carbonation step. The first filter unit is set to separate all the solid components of the suspension stream, which contain both inert components originally present in the waste particles as well as any additional precipitated materials like gypsum and calcium hydroxide, depending on the specific flow sheet. The second filter is represented as a separations unit where the precipitated calcium carbonate is separated as its own stream as well a stream of unreacted CO_2. This CO_2 in reality would be a product of the carbonation vessel, but was represented in the separations unit due to the limitations of the STOICH block.

A splitting block is used to represent the recycle of solvent back to the leaching unit and the remaining discarded waste stream. The recycle flow is described using two separated streams, a recycle-out of the splitter and a recycle-in to the leacher. While it is possible to represent a recycle stream in Aspen using a single connection, convergence issues can quickly arise if error tolerance standards are not met. This disconnected stream approach uses iteration as a means of approximate convergence. The recycle-out stream composition is copied into the recycle-in stream and the simulation is executed

once more. This procedure is then repeated several times until mass compositions are in agreement with mass discrepancies well under 1%.

Solvent Considerations

In this project, the influence of brine as both a solvent and a calcium source is explored alongside the use of waste particles. However, because brine is naturally acidic and the carbonation process requires basis conditions, the system needs to be supplemented with an additional water stream. In total there will be three streams acting a source of water: the brine stream, the water stream, and the recycled stream from the end of the process. A liquid to solid ratio of 50:1 was chosen as a compromise between efficiency and feed costs. As a consequence, the solid waste input will feed at a rate of 1000 kg/hr with the combined liquid streams equating to a rate 50,000 kg/hr.

The carbonation process naturally depletes the hydroxide concentration in the system and the output stream is highly concentrated with ions. Careful considerations must be taken to ensure that recycling solvent doesn't impact the pH levels of the next iteration of input streams. A recycle flow of 1000 kg/hr was chosen after calculations showed that regardless of the waste composition input the pH level of the aqueous stream was maintained above 8.5, as calcium carbonate begins to dissolve back into solution at pH levels below 8.3.[21]

CHAPTER V

RESULTS AND CONCLUSIONS

Across each of the three flowsheets, sensitivity analyses were performed by varying

calcium weight fractions of the wastes. Subsequently, profit rates were determined given the rate

of product produced through each variation based on feed costs as well as waste disposal costs.

While feed costs differ for each scenario, a general cost scheme was created to approximate the

price of water usage, solid waste disposal, and waste water disposal. A summary of these costs is

seen in Table 3 below.

Table 3 Approximated Water and Disposal costs.

Material	Approximate Cost (USD/metric ton)	Source
Water	1.05	24
Waste Solid	7.00	25
Waste Brine Water	4.19	16

Afterwards, equipment and operating costs were evaluated in order to produce investment

return rates. We will explore each waste individually and then will make recommendations on

how to proceed forward based on the calculated results.

Utilities

One of the main interests going into this project was determining how comminution of

particles would impact the economics of the carbonation process. While the final particle size

was set to be 75 microns across every simulation and waste type, a range of plausible input waste

sizes was examined to see its effect on the grinding utility. A key reason for choosing industrial

waste as an alkaline mineral source was the fact that the particles generally are already at viable

reaction sizes. After evaluation at a few interval ranges, it is clear that the impact on grinding

utility is near identical across the whole considered region. Particles in the size interval 1000-

1050 microns resulted in a grinder electrical usage of 3.54 kW while particles in the interval of

1550-1600 drew a usage of 3.80 kW. This already pushes the boundaries of typical waste particle

sizes and for our purpose can be assumed as the theoretical limit. Aspen built-in economic

evaluation software also gives a theoretical annual utility usage and estimates a value

approximately 470 MWh over an 8000-hour working year. This is equivalent to an approximate

rate of 58.7 kW of power, and at an assumed electrical cost of 12 cents per kWh results in a

utility rate of 7.04 dollars per hour.

Fly Ash Process Evaluation

Fly ash is a special case in this analysis as there are two major calcium components

typically found in this waste. Both calcium oxide and calcium sulfate are major leachable

components that come at a variety of mass fractions. To account for this, a sensitivity analysis

was performed individually for both components. A calcium composition range of 20-55 percent

was analyzed as this represented a plausible range for this waste type. One of the resulting

process flow sheets is shown in Figure 4 with labeled flow rates for each stream. Following the

diagram is Figure 5 through 8 which show the PCC production rate and the resulting profit flow

incorporating all of the costs (utilities, feed, waste) assuming the selling price of $400 per ton of
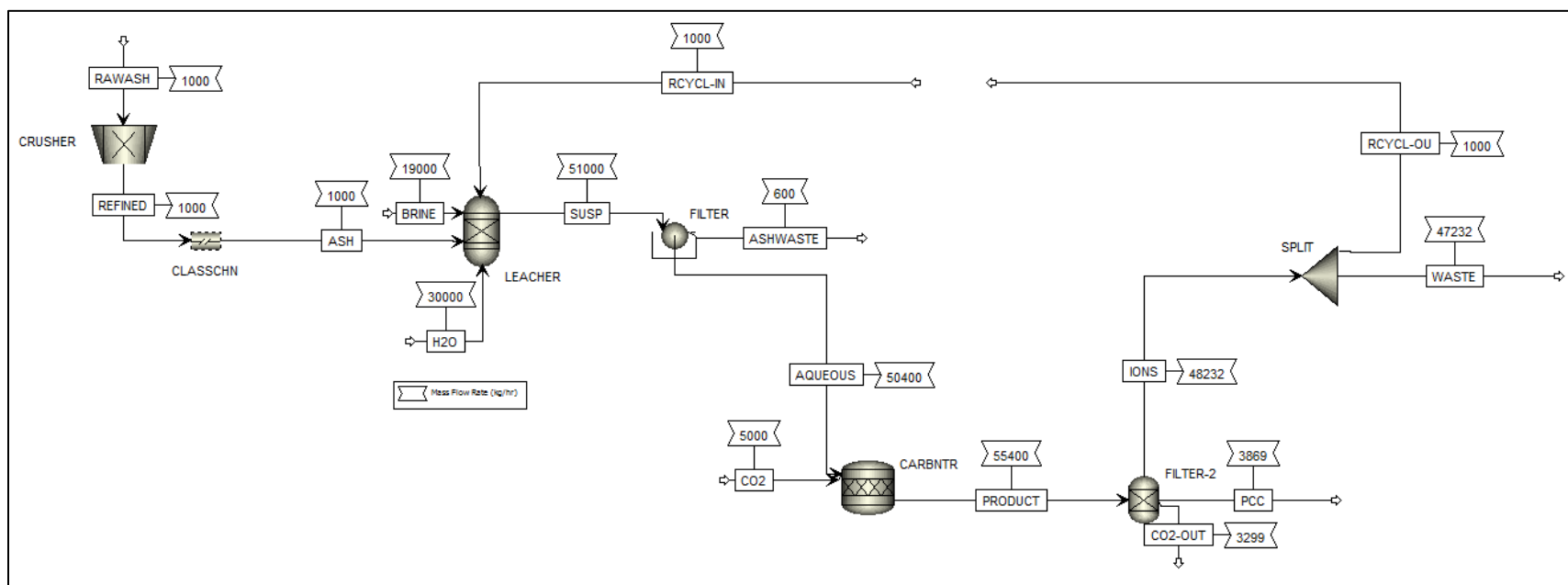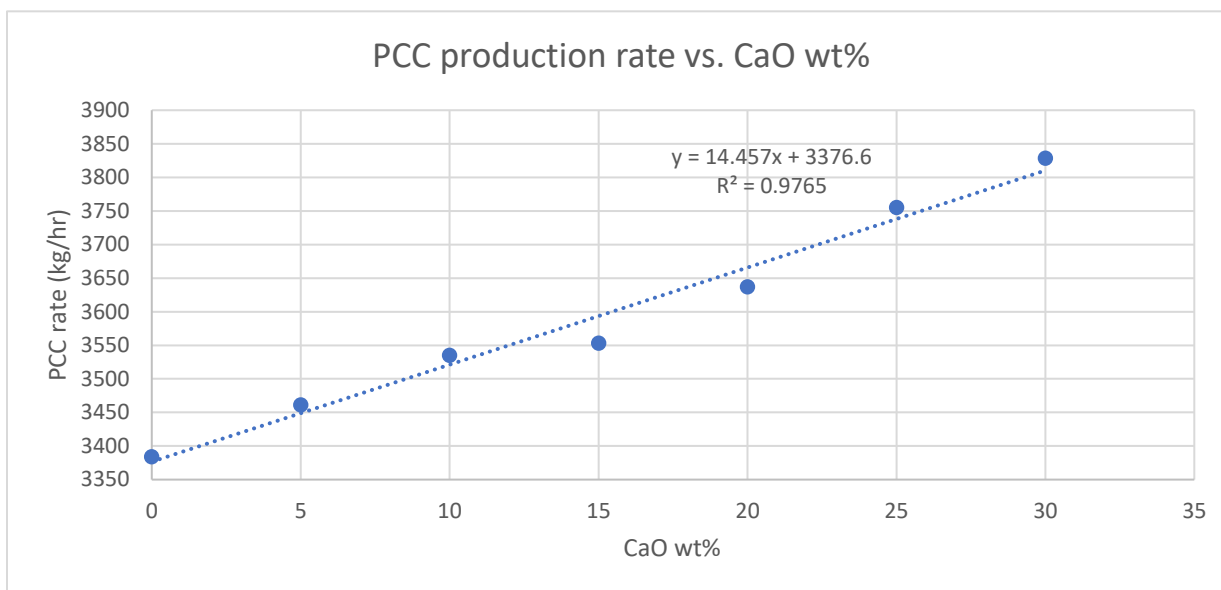
product.

Figure 4 Simulated Waste Ash Flow Results.

Figure 5 Rate of PCC production for varying calcium oxide fractions in fly ash.
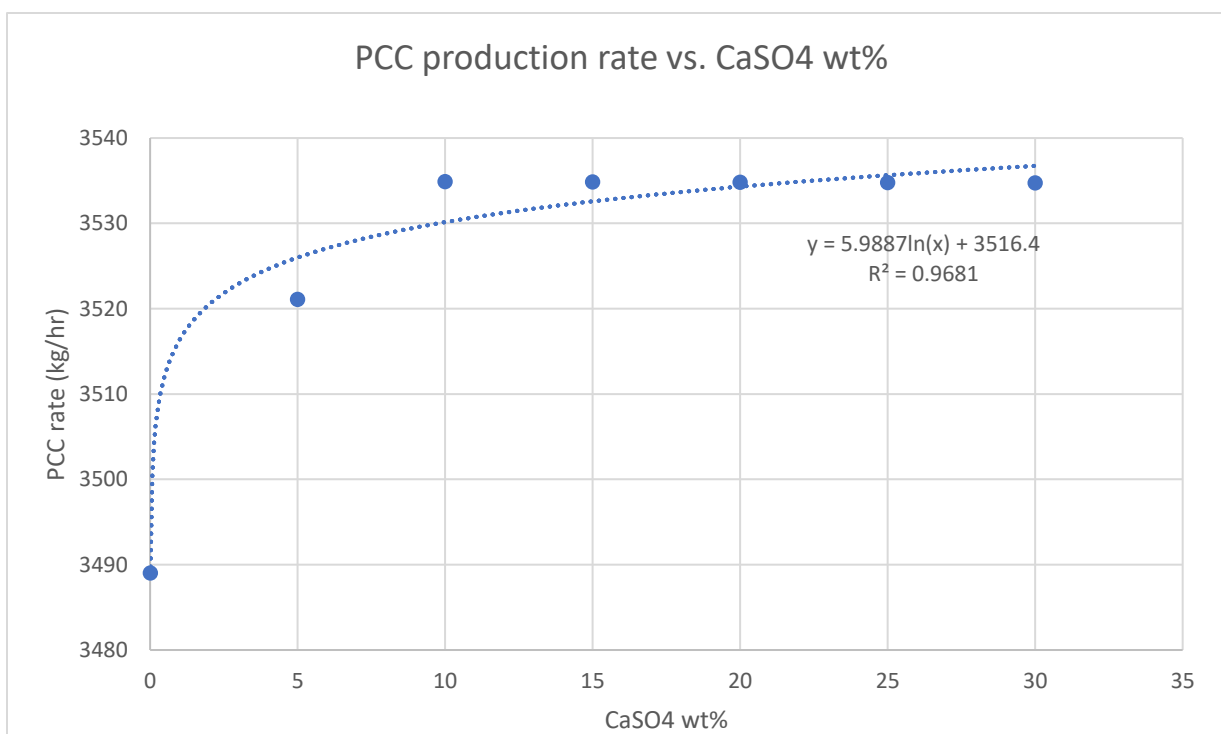

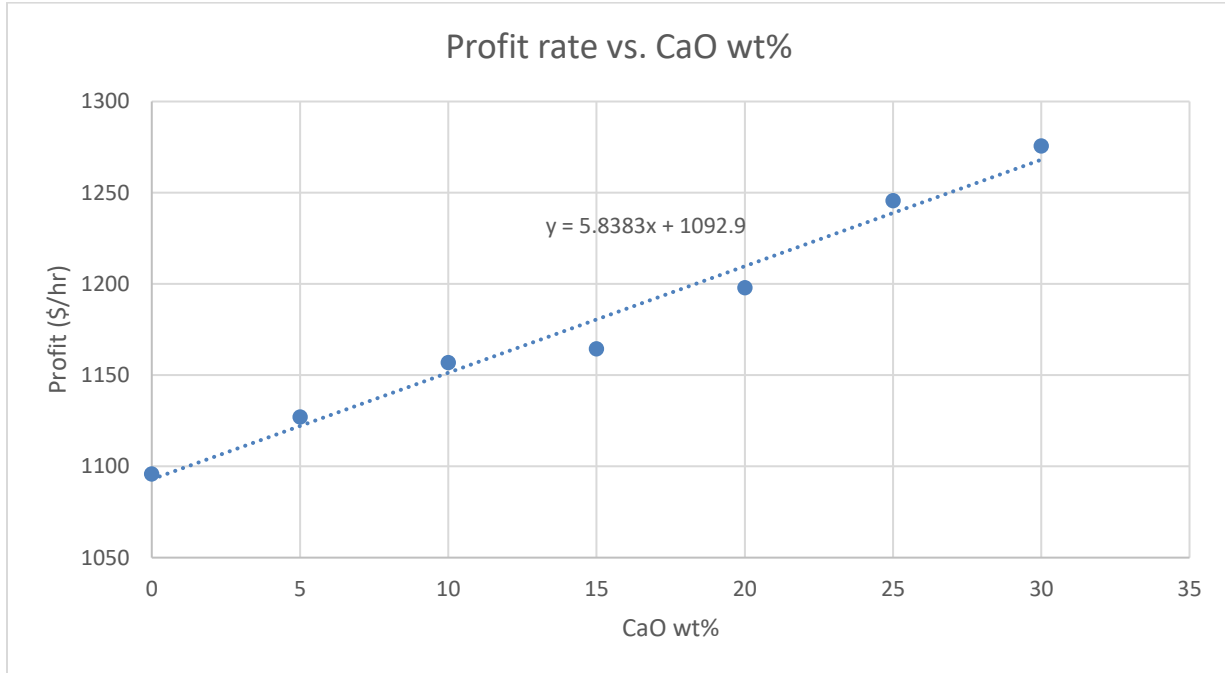**Figure 6 Rate of PCC production for varying calcium sulfate fractions in fly ash.**

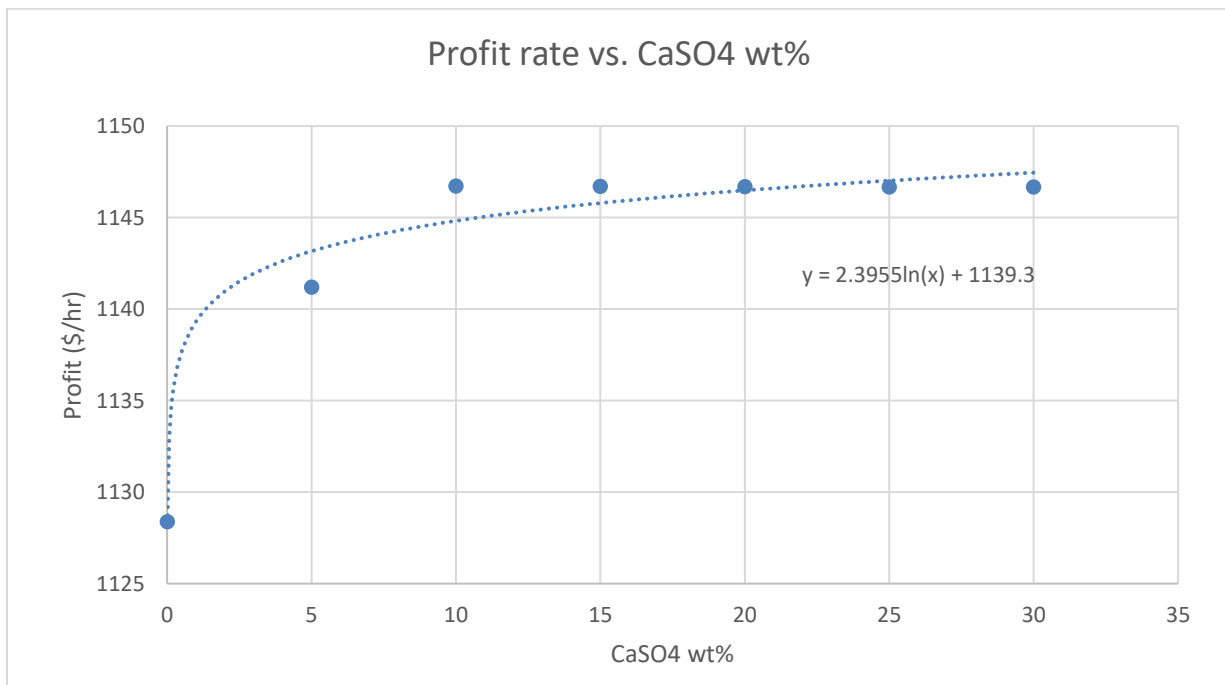**Figure 7 Profit rate of streams for calcium oxide weight fractions in fly ash.**

Figure 8 Profit rate of streams for calcium sulfate fractions in fly ash.

Waste Cement Evaluation

Similar to the fly ash evaluation, a sensitivity analysis was performed by varying the calcium oxide content from a weight percent range of 20-60. The process was performed with the addition of NH_4NO_3 in an amount that would result in a 0.5 M concentration in the leacher (2000 kg/hr). This feed cost was considered in the profit rate analysis with ammonium nitrate assumed to be valued at \$300/ton.[26] An example flow sheet from its simulation is shown in Figure 9 with stream flow rates displayed.
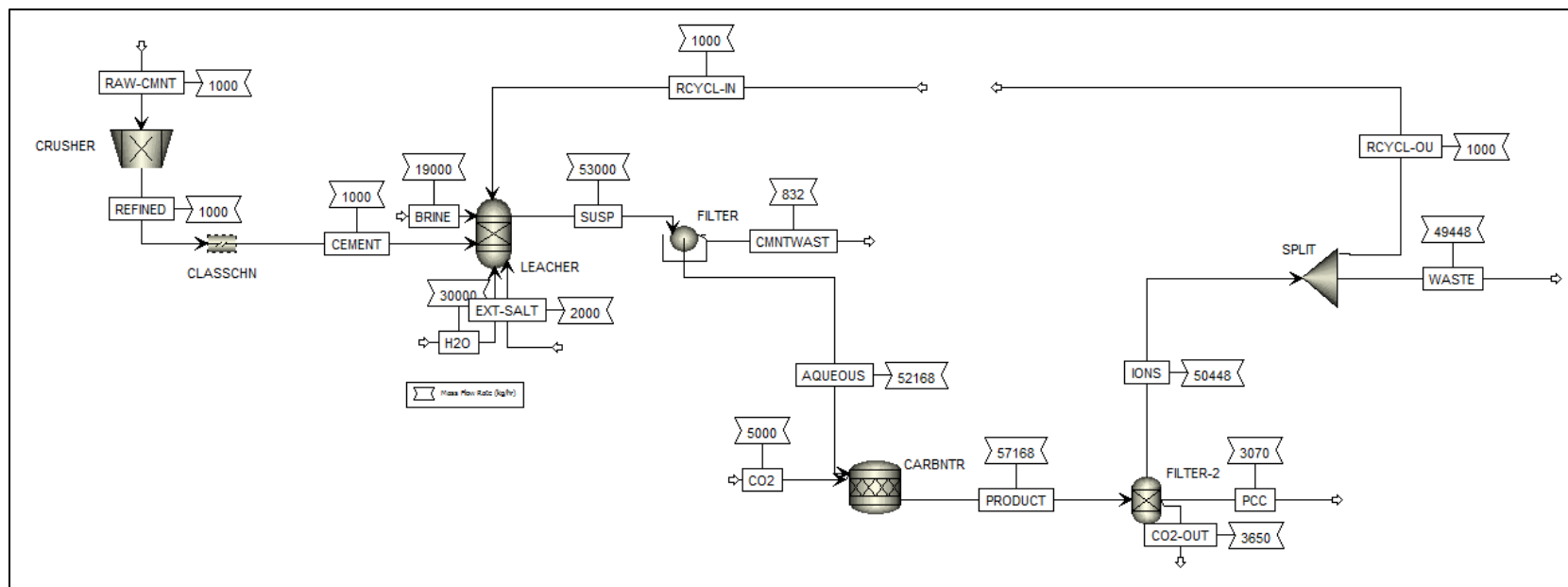
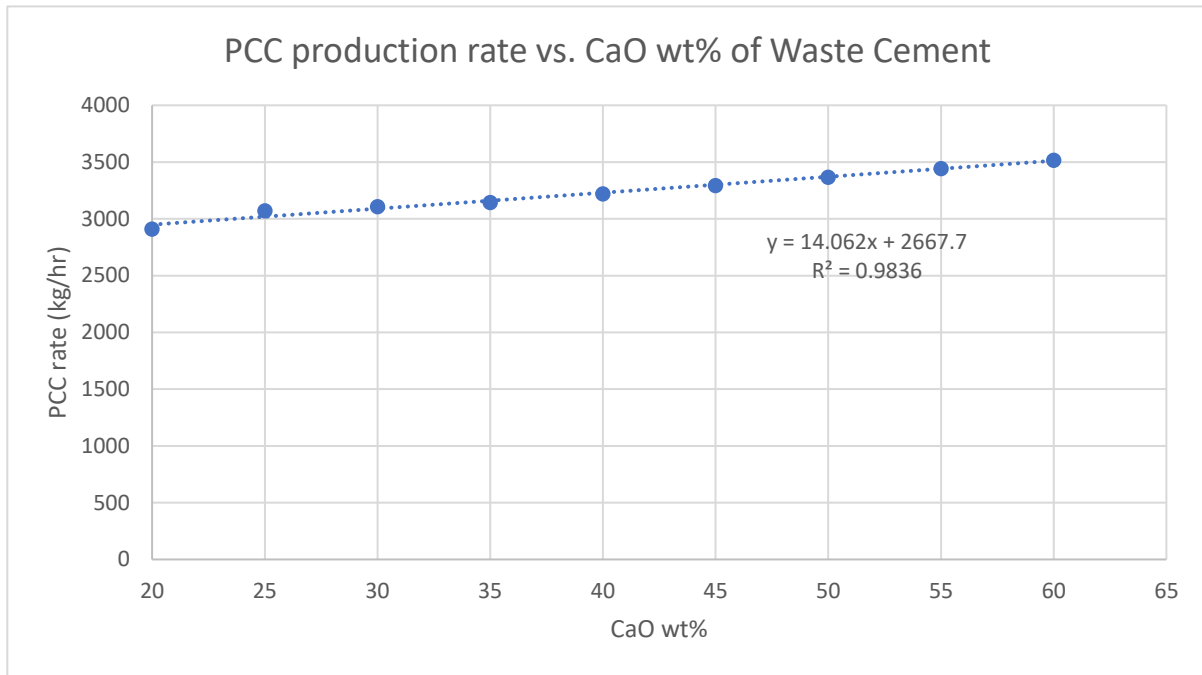**Figure 9 Simulated Waste Cement Flow Results.**

Figure 10 Rate of PCC production for varying calcium oxide fractions in waste cement.
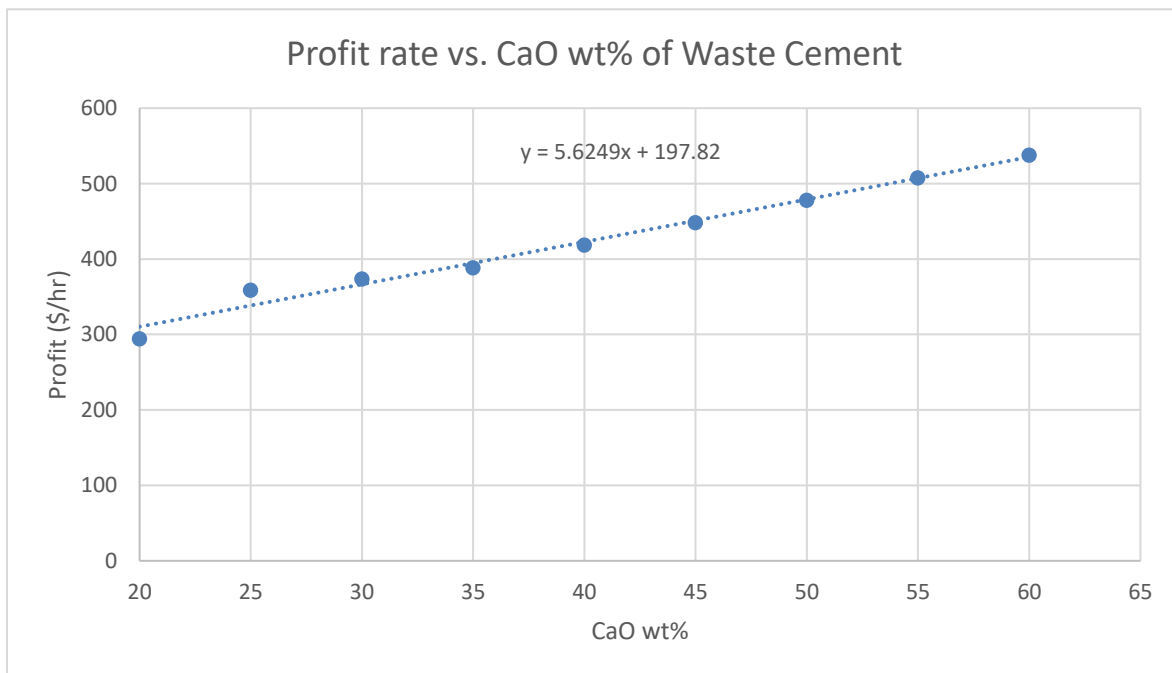
Figure 11 Profit rate of stream for varying calcium oxide fractions in waste cement.

Steelmaking Slag Evaluation

As with the other wastes, the composition of the calcium source was varied, in this case the source is dicalcium silicate. A weight percent range of 20-55 was evaluated and the process included the use of the ammonium salt NH_4Cl. In order to give a concentration of 2.0 M, a flow rate of 5349 kg/hr of salt is needed. This feed cost is considered in the profit analysis, where ammonium chloride is valued at \$130/ton based on current online market prices. An example flow sheet is presented in Figure 12 with stream flows.

Figure 12 Simulated Steelmaking Slag Flow Results.

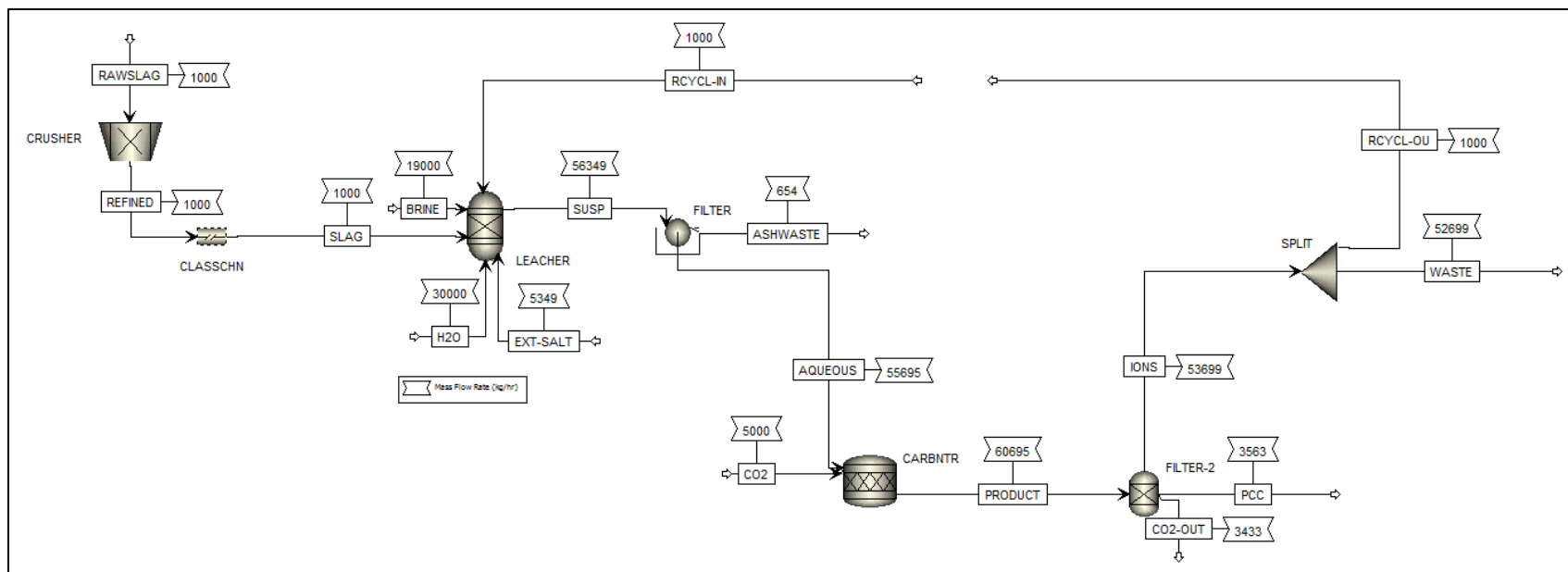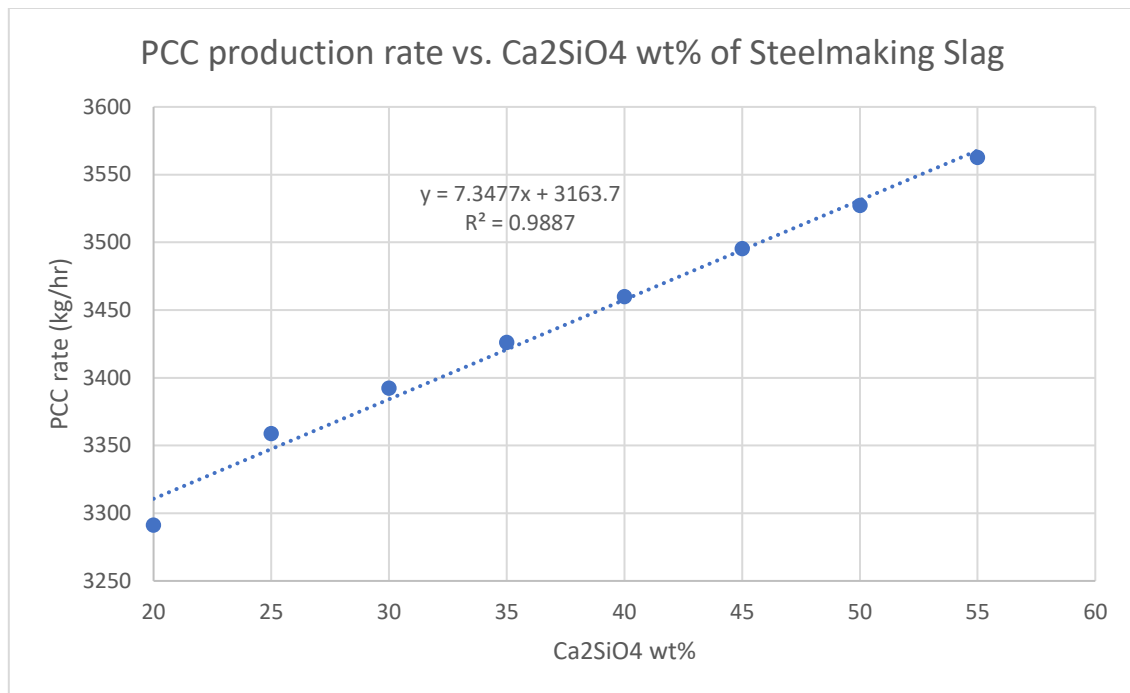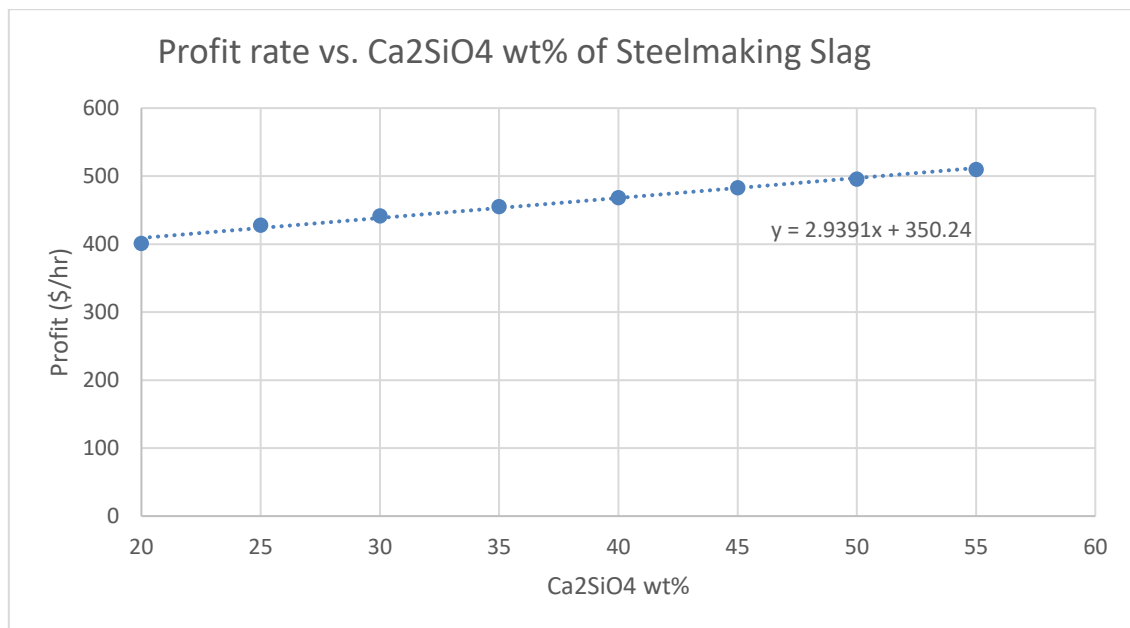**Figure 13 Rate of PCC production for varying dicalcium silicate fractions in steelmaking slag.**

Figure 14 Profit rate of streams for varying dicalcium silicate fractions in steelmaking slag.

Fixed Capital and Investment Return

As a method of approximating the fixed capital cost of the system, installed costs were evaluated for the two reaction vessels. Based on flowrates and residence times, the reactor sizes in this process were estimated as approximately 100 m^3 for the leaching vessel and 60 m^3 for the carbonation reactor. The sixth-tenths factor rule is an approximation used to evaluate the change in installation cost based on a change in equipment size. Using available data for similar agitation vessels, a fixed cost for this process was determined to be $6.9 million.[27] Depreciation costs were taken as a linear depreciation of the fixed capital over a 10 year period. Fixed operating costs include the feed, waste disposal, maintenance, labor, taxes, and insurance. For a similar carbonation process, an approximate maintenance cost of 5% of the fixed capital was used as well as a local tax/insurance cost of 2% of the fixed capital.[28] Assuming a 15% working capital investment (WCI), the total capital investment (TCI) is $8.1 million. The current (2019) corporate tax rate of 21% was also considered. With these values and the calculated profit rates for each stream, return on investment (ROI) calculations can be made to signify how quickly the designed process will pay for itself. Because the fluctuation of pricing for materials can also heavily influence the viability of commercial process, a sensitivity analysis was made for the pricing of the PCC product.

First, it is examined how the fluctuation in PCC pricing affects the profitability of the designed process. As seen in Figure 15, the range of PCC pricing from 200 to 300 dollars per ton is evaluated for all of the absolute minimum calcium mass percentages considered in the previous evaluation sections beforehand. This is done in order to give a

worst-case scenarios in terms of compositions to test how viable this process could be in a real-world implementation. Next, the calculated investment return rate was plotted as a function of PCC selling price and includes both the maximum and minimum calcium components for each waste type in Figure 16.
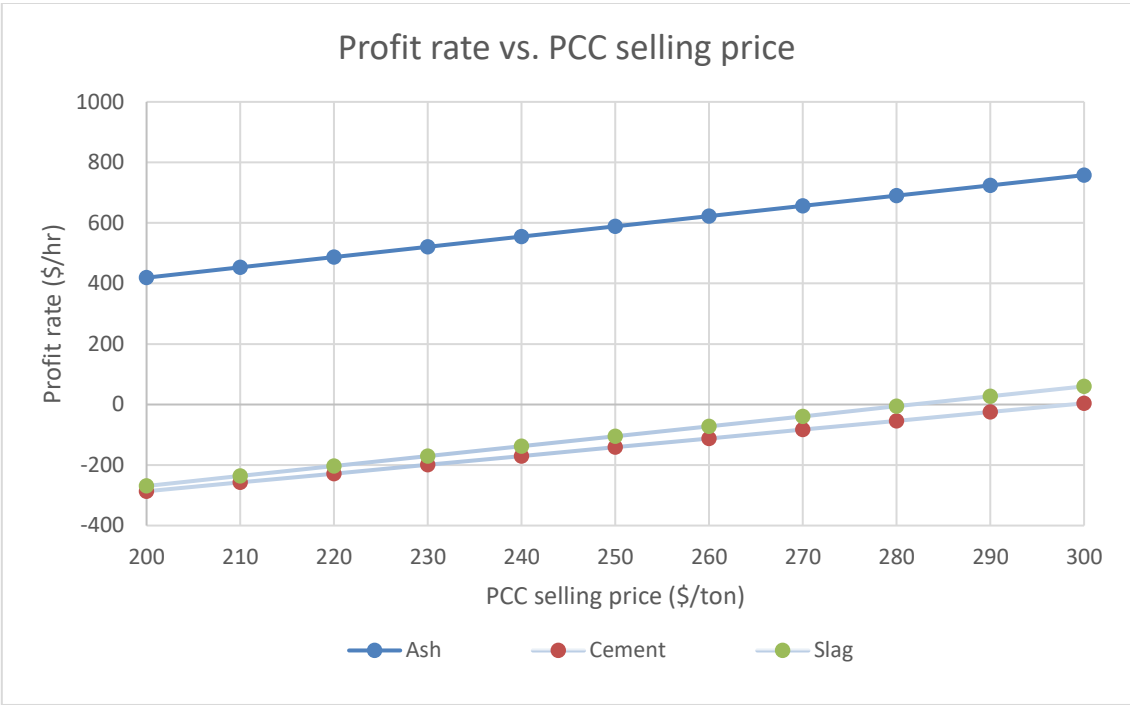
Figure 15 Profit rate for each waste type as a function of product selling price.
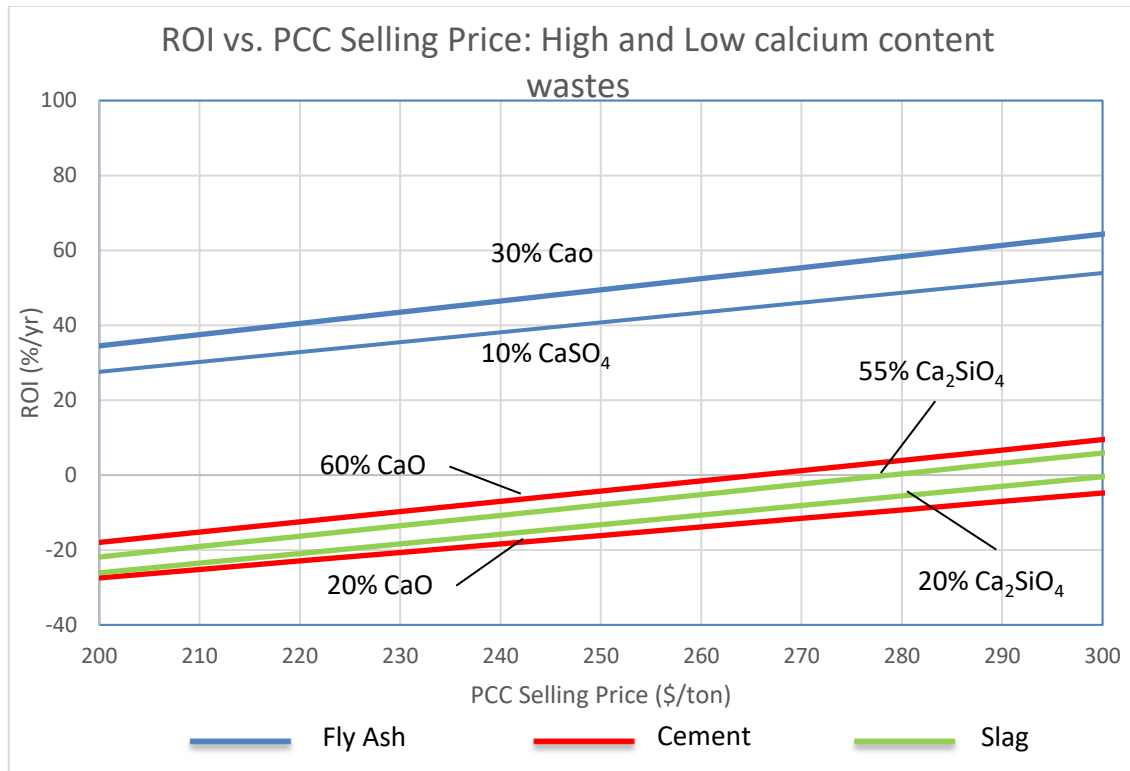
Figure 16 Return on Investment for Both High and Low Calcium Content Wastes as a Function of PCC Selling Price.

Data Interpretation

Initial impressions of Figure 16 suggest that fly ash is a clear choice as an industrial waste feed source for this carbonation process. While its relatively high investment return is encouraging, the other waste sources should not completely be discounted. The cause of this large gap in profitability is by far due to the extra feed costs of the extraction salts used for waste cement and steel slag. While these salts do improve calcium extraction, the high liquid to solid ratio used requires a large input of ammonium salt in order to reach the desired concentration levels. Furthermore, for the systems designed in this project, most of the calcium content is supplied by the fed brine

water. It may prove beneficial to simply neglect the extraction salts and depend on the brine as the major calcium source, however additional bases may be necessary to supplement the alkalinity the leached industrial wastes would be providing. Conversely, the economics of the ammonium salts could be improved by reducing the liquid to solid ratio, however it would need to be investigated how this would impact the rest of the process to determine if this is indeed economically beneficial.

Similar to how a price sensitivity analysis was investigated for PCC, the same could be considered for feed costs, specifically the ammonium salts. Price fluctuations could easily impact the economics of the cement waste and steel slag profitability. Even a small decrease in salt costs could potentially bring the ROI values into a more acceptable range.

Transportation Considerations

For this project, it was assumed CO_2 was available on-site while industrial wastes were transported in from outside sources. It may be beneficial to also look at the case of importing CO_2 to mineralize on-site wastes. A simplified way to compare these is to look at transportation costs for each material. Here we consider the case of the region around the Marcellus Formation where numerous natural gas processing plants are present. A useful map detailing the location of natural gas processing facilities and pipelines in Pennsylvania can be found at http://wikimapping.net/wikimap/gas.html. While many facilities are clustered close around urban regions, transportation between these clusters can range around 300 miles. Around the Pittsburg area, the Eno Transportation Foundation has estimated industrial by-product trucking costs to be about

31.7 cents/ton-mile as of 2006, which would equate to 111.30 USD/ton over a 300 mile distance.[29] An IPCC special report on CO_2 capture and storage estimates CO_2 transportation costs through an onshore pipeline to be approximately 5 USD/ton over a 300 mile distance for an annual mass flow of 6 $MtCO_2$.[30]

Pipelines for natural gas and CO_2 transportation are common existing infrastructures across the U.S. However, it is still useful to look at the situation of installing a new pipeline for the purposes of CO_2 transport. A 2008 Congressional Research Service Report indicated that a steel pipeline of 300 miles would cost about $448 million to install, but is highly variable with steel prices.[31] Compared to the TCI of this project at $8 million, it would be irrational to consider installing a new pipeline solely as a means of sourcing external CO_2.

With these costs in mind, there is a clear advantage with importing CO_2 from outside sources to mineralize on-site wastes rather than importing the wastes if an existing pipeline is present. However, if no existing connection is present or transportation is occurring over a relatively small distance, it is better to import the industrial wastes as was assumed in this project.

Future Work

An opportunity to increase the economic feasibility of using waste cement and steel slag sources for mineralization is available by further investigation into when it is beneficial or disadvantageous to use extraction salts. By optimizing the system to maximize calcium ion content while minimizing liquid/solid ratios and salt usage, profitability could be further increased. Optimization between the three water sources

(water, brine, and recycle) under a minimum pH constraint could also help maximize the recycle ratio in order to decrease fresh water costs and decrease waste water output. Finally, the solid wastes in this project were simplified down to the most common components with only major leachable components and reactions being considered. A more detailed waste description and reaction scheme could improve simulation accuracy and results.

Concluding Remarks

Mineralization is a relatively new consideration for carbon dioxide sequestration. While the benefits of long-term storage and value-added product potential have made it a compelling pathway for utilization, hurdles still remain that have kept it from becoming a major solution to the challenges of CO_2 reduction. It has been said that current knowledge of mineralization is insufficient to conclude if the process is energetically and economically feasible.[32] Hopefully, this work has helped to demonstrate that there is viability for this utilization pathway.

Multiple layers of sustainable opportunities have been merged together to create a unique and practical operation. Carbon dioxide utilization, hazardous waste fixation, and brine water application are independent processes that, with proper integration, could lead to possibilities for creating a greener yet still profitable industrial system.

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APPENDIX A

ADDITIONAL EQUATION DEFINITIONS

Sixth-Tenths Factor Scaling Rule

$$Unit\ A\ Cost = Unit\ B\ Cost * \left(\frac{Unit\ A\ Size}{Unit\ B\ Size}\right)^{0.6}$$

Total Capital Investment

$$TCI = WCI + FCI$$

$$WCI = \frac{0.15}{0.85} * FCI$$

Return on Investment

$$ROI = \frac{Annual\ Net\ (After-Tax)\ Profit}{TCI}$$

$$Annual\ Net\ (After-Tax)\ Profit$$
$$= (Annual\ Sales - AFC - AOC) * (1 - Tax\ Rate) + Depreciation$$