CARBON DIOXIDE AND WATER SPECIATION IN HYDRATED CEMENTS A FOCUS ON SUSTAINABILITY

By

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ABSTRACT

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Concrete, the most used building material in the world contributes to the carbon dioxide releases significantly in the manufacturing of cement, both from the calcinations chemical process and from energy use. But concrete can reabsorb carbon dioxide by carbonation process in which the hydrated cements react with carbon dioxide to form solid calcite. Many researchers have investigated the carbonation under different circumstances for the carbon absorption potential by concrete. Recently, novel concrete mixes are being adopted to address many environmental concerns, and one of these is pervious concrete. With its large surface areas exposed to ambient air, the reactions within pervious concrete are complex. Past concrete chemistry studies interpreted experimental data based on traditional concrete – use analyses, but these interpretations need alterations to include modified reaction kinetics and equilibriums within these novel uses which have different environmental exposure. This research focuses on the carbon dioxide and water speciation in concrete, specifically on other carbon dioxide sequestration species and on how water sequestration in the hydrated cement paste might vary for novel uses of concrete such as pervious concrete with high exposure to ambient air. Temperature Programmed Desorption (TPD) was used to analyze early age cement samples

under various environmental conditions. It was shown that significant amounts of carbon dioxide species other than calcium carbonate do exist in cement paste samples with respect to the stoichiometric potential for reversing the calcination process. It was found that there was a substantial decrease in the formation of calcium hydroxide in the samples representing these novel uses exposed to ambient environmental conditions as compared to traditional early age cement samples.

TABLE OF CONTENTS

ACKNOWLEDGMENT	ii
ABSTRACT	iii
LIST OF TABLES	viii
LIST OF FIGURES	ixx
CHAPTER 1: INTRODUCTION	1 -
1.1 Background on Concrete and CO ₂	1 -
1.2 Background on Sustainable Concrete Uses	5 -
1.3 Research Goals and Significance	6 -
1.4 Current Experimental Methods to Study Carbon and Water Forms in Concrete	7 -
CHAPTER 2: EXPERIMENTAL METHODS	12 -
2.1 Hydrated Cement Sample Preparation and Aging	13 -
2.2 Instrumentation	14 -
2.3 TPD Specimen Preparation	18 -
2.4 TPD Procedure	19 -
2.4.1 Calibration Procedure	19 -
2.4.2 Sample Running Procedure	20 -
2.5 TPD Mass Change Verification	26 -
CHAPTER 3: CARBON DIOXIDE ABSORPTION POTENTIAL IN CONCRETE	27 -
3.1 Water and Carbon Dioxide Amperages from TPD Analysis	28 -
3.2 Data Acquisition	30 -
3.3 Results	33 -
3.3.1 Isohydration Curve	33 -

3.3.2 Estimated Percent Carbon Absorption at Lower Temperature Ranges	36 -
3.3.3 Repeatability of the Experiments	42 -
3.4 Discussions	43 -
3.4.1 Impact of Sample Size on Desorption Rate	43 -
3.4.2 Sample Mass Variations While Aging	44 -
3.4.3 The Mass Change Verification Analysis	45 -
3.4.4 Percent Carbon Absorption	46 -
CHAPTER 4: EARLY AGE CALCIUM HYDROXIDE FORMATION IN NOVEL	
SUSTAINABLE CONCRETE USES	50 -
4.1 Water Amperages from TPD	51 -
4.2 Data Acquisition	53 -
4.3 Results	55 -
4.3.1 Statistical Data on Water Desorption Spikes	55 -
4.3.2 Water Desorption Hydrolysis Results	56 -
4.3.3 Calcium Hydroxide Formation	57 -
4.4 Discussions	61 -
4.4.1 Statistical Analysis on Ca(OH) ₂ Frequency	61 -
4.4.2 Water Desorption Hydrolysis Analysis	62 -
4.4.3 Calcium Hydroxide Formation Analysis	63 -
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS	66 -
NOTATION	69 -
REFERENCES	71 -
APPENDICES	75 -

APPENDIX 1: CALIBRATION FOR CONSISTENCY 70	6 -
APPENDIX 2: CALIBRATION FOR DATA ANALYSIS 78	8 -
A2.1 Correction Factor Method 78	8 -
A2.2 RF (Response Factor) Method	1 -
APPENDIX 3: WATER AND CARBON DIOXIDE DESORPTION CURVES	4 -

LIST OF TABLES

Table 1.1: Temperature Ranges in Current Studies	11 -
Table 3.1: Different Percent CO ₂ Absorption Based on Different Percent CO ₂ Left after the	
TPD Analysis at Lower Temperature Ranges (<550°C)	34 -
Table 3.2: Results from the TPD Experiments for Samples Heated to 550°C with Assumed Lo	w
Levels of Carbonation	37 -
Table 3.3: Results from the TPD Experiments for Samples Heated to 550°C with Assumed	
Higher Levels of Carbonation	38 -
Table 3.4: Results from the TPD Experiments for Samples Heated to 550°C	39 -
Table 3.5: Results from the TPD Experiments for Samples Heated to 700°C	40 -
Table 3.6: Standard Deviation of Two Sets of Samples with Final Temperature of 550°C to Te	est
Repeatability of TPD Analysis	42 -
Table 4.1: Presence of Second Water Desorption Spike in Open Samples	56 -
Table 4.2: Presence of Second Water Desorption Spike in Covered Samples	56 -
Table 4.3: Water Desorption Masses for Paired Samples at Different Ages.	58 -
Table 4.4: Average Mole Ratios of Ca(OH) ₂ to CaO in Covered Cement Samples	60 -
Table 4.5: Analysis of Open Samples with Second Water Spikes.	62 -
Table A1.1: Calibration for Consistency Based on RF Results.	77 -
Table A2.1: Results of Samples Used for Calibration Process.	79 -
Table A2.2: Iteration for the Correction Factor from Published Data. -	81 -
Table A2.3: Verification of RF for H ₂ O from Other Users	83 -

LIST OF FIGURES

Figure 2.1: Flow scheme of the Temperature Programmed Desorption (TPD) system 16 -
Figure 2.2: Temperature Programmed Desorption (TPD) system setup
Figure 2.3: Pyrex reactor (a) and quartz reactor (b) for TPD analysis
Figure 2.4: Output of Tware32 for a cement sample 23 -
Figure 3.1: Water and CO ₂ desorption curves for sample AOX31PW 29 -
Figure 3.2: Water and CO ₂ desorption curves for sample AC7W 29 -
Figure 3.3: Isohydration Diagram for cement with 61 mass percent CaO 35 -
Figure 3.4: Isohydration Diagram for cement with 61 mass percent CaO lower portion 41 -
Figure 3.5: Comparison of normalized mass of ¹ / ₄ in covered and open samples for both
ambient and oven 44 -
Figure 4.1: Water desorption curves for typical ambient open (AO) and oven open (OO)
samples 51 -
Figure 4.2: Water desorption curves for typical ambient covered (AC) and oven covered (OC)
samples 52 -
Figure 4.3: Typical water desorption curve depicting areas of different temperature ranges and
desorption phenomena of interest (Sample ACXX6Pb) 54 -
Figure 4.4: Mole fraction of calcium hydroxide to calcium oxide in covered cement samples 61 -
Figure A1.1: RF calibration on TPD system on June 30 th , 2008 76 -
Figure A2.1: Response factor calibration method for TPD analysis on July 2 nd , 2008 82 -
Figure A3.1: Water and CO ₂ desorption curves for sample AC7C 84 -
Figure A3.2: Water and CO ₂ desorption curves for sample AC7W 85 -
Figure A3.3: Water and CO ₂ desorption curves for sample AO8C

Figure A3.4: Water and CO ₂ desorption curves for sample AO8W.	86 -
Figure A3.5: Water and CO ₂ desorption curves for sample ACXX7PC	86 -
Figure A3.6: Water and CO ₂ desorption curves for sample ACXX7PW	87 -
Figure A3.7: Water and CO ₂ desorption curves for sample AOX31PC	87 -
Figure A3.8: Water and CO ₂ desorption curves for sample AOX31PW	88 -
Figure A3.9: Water and CO ₂ desorption curves for sample AC8W	88 -
Figure A3.10: Water and CO ₂ desorption curves for sample AO9C.	89 -
Figure A3.11: Water and CO ₂ desorption curves for sample AO9W.	89 -
Figure A3.12: Water and CO ₂ desorption curves for sample ACXX9PC	90 -
Figure A3.13: Water and CO ₂ desorption curves for sample ACXX9PW	90 -
Figure A3.14: Water and CO ₂ desorption curves for sample AOX36PC.	91 -
Figure A3.15: Water and CO ₂ desorption curves for sample AOX36PW.	91 -
Figure A3.16: Water and CO ₂ desorption curves for sample OO18WD.	92 -
Figure A3.17: Water and CO ₂ desorption curves for sample OO18WN.	92 -
Figure A3.18: Water and CO ₂ desorption curves for sample OO19WD.	93 -
Figure A3.19: Water and CO ₂ desorption curves for sample OO19WN	93 -
Figure A3.20: Water and CO ₂ desorption curves for sample OO20WD	94 -
Figure A3.21: Water and CO ₂ desorption curves for sample OO20WN.	94 -
Figure A3.22: Water and CO ₂ desorption curves for sample OO21WD	95 -
Figure A3.23: Water and CO ₂ desorption curves for sample OO21WN	95 -
Figure A3.24: Water and CO ₂ desorption curves for sample OOX31PWD	96 -
Figure A3.25: Water and CO ₂ desorption curves for sample OOX31PWN.	96 -
Figure A3.26: Water and CO ₂ desorption curves for sample OOX32PWD.	97 -

Figure A3.27:	Water and CO ₂ desorption curves for sample OOX32PWN	97 -
Figure A3.28:	Water and CO ₂ desorption curves for sample OOX33PWD	98 -
Figure A3.29:	Water and CO ₂ desorption curves for sample OOX33PWN	98 -
Figure A3.30:	Water and CO ₂ desorption curves for sample OOX34PWD	99 -
Figure A3.31:	Water and CO ₂ desorption curves for sample OOX34PWN	99 -
Figure A3.32:	Water and CO ₂ desorption curves for sample OO27WD 1	100 -
Figure A3.33:	Water and CO ₂ desorption curves for sample OO27WN 1	- 00
Figure A3.34:	Water and CO ₂ desorption curves for sample OO28WD 1	101 -
Figure A3.35:	Water and CO ₂ desorption curves for sample OO28WN 1	101 -
Figure A3.36:	Water and CO ₂ desorption curves for sample AOX32PWD 1	102 -
Figure A3.37:	Water and CO ₂ desorption curves for sample AOX32PWN 1	102 -
Figure A3.38:	Water and CO ₂ desorption curves for sample AOX33PWD 1	103 -
Figure A3.39:	Water and CO ₂ desorption curves for sample AOX33PWN 1	103 -
Figure A3.40:	Water and CO ₂ desorption curves for sample AOX34PWD 1	104 -
Figure A3.41:	Water and CO ₂ desorption curves for sample AOX34PWN 1	104 -
Figure A3.42:	Water and CO ₂ desorption curves for sample AOX35PWD 1	105 -
Figure A3.43:	Water and CO ₂ desorption curves for sample AOX35PWN 1	105 -
Figure A3.44:	Water and CO ₂ desorption curves for sample AOX71FWD 1	106 -
Figure A3.45:	Water and CO ₂ desorption curves for sample AOX71FWN 1	106 -
Figure A3.46:	Water and CO ₂ desorption curves for sample AOX72FWD 1	107 -
Figure A3.47:	Water and CO ₂ desorption curves for sample AOX72FWN 1	107 -
Figure A3.48:	Water and CO ₂ desorption curves for sample AOX73FWD 1	108 -
Figure A3.49:	Water and CO ₂ desorption curves for sample AOX73FWN	108 -

Figure A3.50: Water and CO ₂ desorption curves for sample AOX74FWD 109 -
Figure A3.51: Water and CO ₂ desorption curves for sample AOX74FWN 109 -
Figure A3.52: Water and CO ₂ desorption curves for sample ACXX6Pa 110 -
Figure A3.53: Water and CO ₂ desorption curves for sample ACXX6Pb 110 -
Figure A3.54: Water and CO ₂ desorption curves for sample ACXX8Pa 111 -
Figure A3.55: Water and CO ₂ desorption curves for sample ACXX8Pb 111 -
Figure A3.56: Water and CO ₂ desorption curves for sample AOX37Pa 112 -
Figure A3.57: Water and CO ₂ desorption curves for sample AOX37Pb 112 -
Figure A3.58: Water and CO ₂ desorption curves for sample AOX38Pa 113 -
Figure A3.59: Water and CO ₂ desorption curves for sample AOX38Pb 113 -
Figure A3.60: Water and CO ₂ desorption curves for sample OCXX6Pa 114 -
Figure A3.61: Water and CO ₂ desorption curves for sample OCXX6Pb 114 -
Figure A3.62: Water and CO ₂ desorption curves for sample OCXX8Pa 115 -
Figure A3.63: Water and CO ₂ desorption curves for sample OCXX8Pb 115 -
Figure A3.64: Water and CO ₂ desorption curves for sample OOX36Pa 116 -
Figure A3.65: Water and CO ₂ desorption curves for sample OOX36Pb 116 -
Figure A3.66: Water and CO ₂ desorption curves for sample OOX38Pa 117 -
Figure A3.67: Water and CO ₂ desorption curves for sample OOX40PWD 117 -
Figure A3.68: Water and CO ₂ desorption curves for sample OOX39PWN 118 -
Figure A3.69: Water and CO ₂ desorption curves for sample OOX39PWD 118 -
Figure A3.70: Water and CO ₂ desorption curves for sample AOX40PWN 119 -
Figure A3.71: Water and CO ₂ desorption curves for sample AOX40PWD 119 -
Figure A3.72: Water and CO ₂ desorption curves for sample AOX39PWD 120 -

CHAPTER 1 INTRODUCTION

Concrete is the most widely used building material in the world because of its strength and durability among other benefits. Concrete is used in almost every type of construction, and in an era of increased attention on the environmental impact of construction, concrete performs well when compared to other building materials. The amount of carbon dioxide (CO_2) produced during manufacturing and the net impact of using concrete as a building material is relatively small. However, when it comes to sustainable development, there is always opportunity for improvement.

1.1 Background on Concrete and CO₂

The threat of climate change is considered to be one of the major environmental challenges for our society. Carbon dioxide is one of several green house gases that can cause global warming by trapping the sun's radiant energy in our atmosphere, and this process is called greenhouse effect. CO_2 exists in relatively small amounts (380 ppm) in the atmosphere.

Concrete is a composite material consisting of aggregates, a binder phase and additives. The binder phase (hardened cement paste) is formed by the reaction (hydration) of Portland cement clinker with water. Cement, one of the major ingredients of concrete, is made from calcium oxide (CaO) as well as other ingredients such as clays, various oxides and impurities. Typically, CaO makes up 60-65% (by weight) of the cement mass (Mehta and Monteiro 1993). When water is mixed with cement, a series of complex reactions is initiated. It is expected that CaO will form Ca(OH)₂ (Equation 1.1) which contributes to the alkalinity of the cement.

$$CaO_{(s)} + H_2O_{(l)} \to Ca(OH)_{2(s)}$$

$$\tag{1.1}$$

In traditional concrete uses, the main strength-giving compounds are the calcium silicates which react with water to produce a calcium silicate hydrate gel. Note the unique nomenclature used in concrete chemistry and expressed in Equation 1.2, where 'C', 'S' and 'H' represent the oxides of calcium, silicon and hydrogen (water) respectively (Mehta and Monteiro 1993).

$$C_x S_y + z H \to C_x S_y H_z \tag{1.2}$$

The manufacturing process of cement contributes to the emission of CO_2 through the combustion of fossil fuels, as well as through the decarbonization of limestone. Because of the dominant use of carbon-intensive fuels, such as coal in clinker making, the cement industry is a major source of CO_2 emissions. The worldwide contribution from the concrete industry to the anthropogenic CO_2 load is estimated to exceed 5% (Pade and Guimaraes 2007). Roughly half of the emitted CO_2 originates from combustion of the fuel and half originates from the conversion of the raw material in the calcination process (Equation 1.3).

$$CaCO_{3(s)} \to CaO_{(s)} + CO_{2(g)} \tag{1.3}$$

Total global cement production in 2005 was 2300 Mt (2535 million tons), and U.S. cement manufacturing capacity is 4.3% of global capacity (USGS). According to EPA, between 900 and 1100 kg (1984 and 2425 lbs) of CO_2 is emitted for every 1000 kg (2205 lbs) of Portland cement produced in the U.S. This depends on the fuel type, raw ingredients used and the energy efficiency of the cement plant (EPA 2005). According to the most recent survey of Portland Cement Association (PCA) members, an average of 927 kg (2044 lb) of CO_2 is emitted for every 1000 kg (2205 lb) of Portland cement produced in the US (Marceau et al. 2006). Global CO_2 emissions from cement production (298 million metric tons of carbon in

2004) represent 3.8% of global CO_2 releases from fossil-fuel burning and cement production (Marland et al. 2007).

However, concrete can reabsorb CO_2 during the product life cycle through a process called carbonation and other opportunities for carbon sequestering in concrete (Gajda 2001). Due to the dissociation of various hydroxides as demonstrated by Equation 1.4, concrete typically has a high pH. If the cement paste is exposed to CO_2 in the air (CO_{2g}) under certain humidity conditions, the $Ca(OH)_2$ can dissociate and the CO_{2g} can dissolve ($H_2CO_3^*$), then a series of reactions resulting in the reverse reaction to calcination, carbonation, are known to take place (Equations 1.5-1.9). A simplification of these carbonation reactions is as follows:

1) Dissociation of Ca(OH)₂

$$Ca(OH)_2 \to Ca^{2+} + 2OH^- \tag{1.4}$$

2) Atmospheric CO₂ dissolution

$$CO_{2(g)} + H_2O \to H_2CO_3^* \tag{1.5}$$

3) Formation of carbonic acid

$$H_2 CO_3^* \to H_2 CO_3 \tag{1.6}$$

4) Dissociation of carbonic acid to hydrogen and bicarbonate ions

$$H_2CO_3 \to H^+ + HCO_3^- \tag{1.7}$$

5) Dissociation of bicarbonate ions to hydrogen and carbonate ions

$$HCO_3^{-} \to H^+ + CO_3^{2-} \tag{1.8}$$

6) Formation of solid calcite

$$Ca^{2+} + CO_3^{2-} \to CaCO_{3(s)} \tag{1.9}$$

This carbonation process in concrete is diffusion limited and dependent on many variables such as relative humidity (water content), pH, concrete mix, concrete age, and pore structure (surface area) (Fukushima et al. 1998; Lagerblad 2005). One research study estimates that between 33% and 57% of the CO_2 emitted from calcination will be reabsorbed through carbonation of concrete surfaces over a 100-year life cycle (Pade and Guimaraes 2007).

It is theoretically assumed herein that significant amounts of CO_2 might also be potentially absorbed in the hydrated phase of concrete. Equations 1.5-1.8 represent typical equilibrium conditions where the various species are balanced based on parameters such as temperature and ionic activity. For hydrated cement, there is also a large concentration of the hydroxide ions in the presence of water as demonstrated by Equation 1.1. As CO_2 dissolves and dissociates as in Equations 1.5-1.9, the hydrogen ions produced would tend to react with the hydroxide ions in the equilibrium producing water as in Equation 1.10.

$$H^+ + OH^- \to H_2 O \tag{1.10}$$

This will encourage more dissolution to keep the system in equilibrium, buffering the system and keeping the pH elevated until the buffering capacity of the $Ca(OH)_2$ (alkalinity) is used up. Then, more dissolution of CO₂ would result in a lower pH which would favor the reactants in Equations 1.5-1.9 over the products. In addition, hydroxide, bicarbonate and carbonate ions in aqueous solutions are known to form complexes with many metal ions such as calcium and magnesium (Ca²⁺, Mg²⁺). Therefore, CO₂ can be potentially absorbed in intermediate forms other than solid calcite in cement paste based on the hydrated chemistry of concrete exposed to CO₂ under certain pH conditions, and also complexation chemistry.

Whilst carbonation during the service life of high strength structural concrete is intentionally kept to a minimum, there is a much greater uptake at the end of its life when it is crushed and CO_2 is more readily absorbed due to the significant increase in surface area (Engelsen et al. 2005). In low strength concrete such as blocks, and cementitious materials such as mortar, carbonation is much more rapid as CO_2 can permeate the material more easily. This does not present a problem since no reinforcing bar is present.

1.2 Background on Sustainable Concrete Uses

As used in everyday speech, sustain means to support or to keep a process going, and the goal of sustainability is that life on the planet can be sustained for the foreseeable future. For construction materials, it is necessary to consider all stages in the life of the material. For the reason of sustainability issues, many modified and novel forms of concrete are being developed to address emerging environmental goals, for example, pervious concrete is a unique paving material which is used for stormwater management and low impact development. Recycled concrete chunks are being used for road bases and pavement aggregates.

Some of the novel forms of concrete have different physical and chemical properties than traditional concrete structures such as walls and slabs, and will therefore react differently over time under ambient conditions during their life cycle. Pervious concrete has an initial lower water content, higher porosity, and large internal surface areas due to its 15-25% void structure (Tennis et al. 2004). Both recycled concrete aggregates (RCA) and recycled concrete fines have much larger exposed surface areas than their primary uses. Concrete chemistry for traditional applications has been studied aggressively over many decades to investigate the reactions of cements to various environments, the chemical reactions of various mix designs and the very dynamic chemical nature of this major construction material. Now there is a need to understand how this chemistry may vary for novel alternative concrete uses, particularly in applications with large exposed surface areas where concrete chemistry and environmental chemistry interact. Of particular interest in this research is the formation of $Ca(OH)_2$ in the early age of some novel concrete uses due to the importance of Equation 1.4 with respect to the carbonation reaction process.

1.3 Research Goals and Significance

The intent of this study was to learn more about concrete chemistry with respect to both CO_2 absorption and new sustainable uses with different environmental exposures in terms of CO_2 and water speciation. The two specific goals are:

(1) CO_2 Speciation

One objective of this research is to prove that there is a potential for significant amount of CO_2 absorption in intermediate hydrated forms within the cement paste in concrete in addition to the 'final' carbonation product of calcite. This is important for understanding the overall carbon footprint and equilibrium and kinetics of CO_2 absorption in concrete, which might give us addition idea when searching ways to mitigate CO_2 issues.

The kinetics of CO_2 absorption is dependent on many factors such as carbon dioxide exposure and relative humidity in the air or soil. It is also dependent on the chemistry of the concrete sample which is being exposed to these environmental conditions. Quantifying the ability of pervious concrete and other novel concrete uses to sequester carbon dioxide over their product lifetimes would help a lot with respect to sustainability. For example, if 5% to 10% of CO_2 is absorbed or embodied in the concrete in addition to carbonation process, then approximately 100 to 300 kg of CO_2 is embodied for every cubic meter of concrete, which is about 15 to 30 million metric tons of carbon released every year globally.

(2) H_2O Speciation

The other objective is to document the impact that environmental conditions might have on the early age formation of calcium hydroxide (Ca(OH)₂) in novel cement and concrete mixes in contact with the ambient environment as compared to traditional concrete uses, especially the variations that may occur as cement is exposed to an ambient 'carbonating' environment with air and most importantly, carbon dioxide. This project focuses on how water sequestration in the hydrated cement paste might vary under the different conditions for novel uses of concrete with high exposure to ambient air where the traditional formation of Ca(OH)₂ might be altered by competition for the CaO site by CO₂ and the lower levels of water within the paste. This might help us to better understand the speciation of the chemical equilibrium in the cement paste and might further explain the major ingredient for carbonation or CO₂ absorption in the hydrated cement pastes associated with these uses is critical to understanding carbon sequestration.

1.4 Current Experimental Methods to Study Carbon and Water Forms in Concrete

Various experimental methods are available to evaluate the carbonation in the concrete. The most well known and easiest method is a pH indicator like phenolphthalein sprayed on the freshly broken surface of a given concrete sample. Based on this approach, it is possible to define a depth of carbonation related to the pH value of the interstitial solution. Some observations of these fresh fractures under optical or scanning electron microscopes reveal different forms of calcium carbonates and carbonated C-S-H. X-ray diffraction and infrared spectrometry detect the presence of various chemical compounds which are typical of virgin or

carbonated concrete (portlandite, C-S-H, calcite, vaterite, and aragonite) in a crushed sample of hydrated cement paste. The proportioning of carbon and oxygen isotopes applied to carbonated concrete quantifies the calcite formed during the carbonation by extracting the CO_2 from a small sample of hydrated cement pastes and afterwards by proportioning the gaseous isotopes in a mass spectrometer. Thermo-gravimetric analysis (TGA), which quantifies the portlandite and the calcium carbonates resulting from carbonation, is generally applied to hydrated cement pastes and concrete. In TGA, a sample is slowly heated, and the rate of temperature change or the mass change is recorded over time. These changes over various temperature ranges are then attributed to specific chemical and physical processes and the release of associated gases, such as H₂O and CO₂. Another method combining a thermal decomposition of carbonates and an infrared analysis of the extracted gases enables the determination of the CO_2 concentration in mortar samples that are reduced into powder. These three latter methods are quantitative and provide carbonation profiles as a function of depth (Villain et al. 2007).

Many researchers have investigated the different forms of water and carbonation in different types of concrete samples under various conditions, and many of the studies are based on using Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA). Classic studies on hydrated Portland cement were performed by Cole and Kroone (1960). They attributed a low-temperature endothermic spike at about 500°C to the dehydration of Ca(OH)₂. Also, they found that most of the CO₂ was in various calcium carbonate forms and they gave two areas of calcite decomposition: (1) a poorly crystallized spike (600-750°C), and (2) a well crystallized spike (820°C). However, they deduced that there was a significant amount of CO₂ 'loosely' held in the mortar and released slowly upon heating.

Taylor et al. (1985 and 1985a) studied various cement samples with pure cement and with other cementitious materials (fly ash and slag) using TGA. The cement samples were carefully prepared in nitrogen environments and sealed to limit exposure to carbon dioxide in the air. Based on their results, they assumed that the mass releases between approximately 400- 650° C were predominantly due to water which was a result of the breaking of the Ca(OH)₂ bonds and some other oxide phases. The mass releases between $650-750^{\circ}$ C were due to the CaCO₃ decomposition, and the total amount of CaCO₃ in all the samples ranged 0-2% by volume.

Papadakis et al. (1992) performed TGA and X-ray analysis on carbonated and noncarbonated cement specimens and found that the temperature range around 460° C was predominantly Ca(OH)₂ desorption in the noncarbonated samples. Prior to that, they displayed that Ca(OH)₂ decomposition between 400-500°C and CaCO₃ decomposition between 600-800°C (Papadakis et al. 1991).

Chang et al. (1993) examined ordinary concrete samples made from the most common Portland Type I cement as well as some uncommon glossy looking concrete lumps (collected from a real fire scene) by using thermal gravity analysis (TGA), differential thermal analysis (DTA), and other instrumental methods with the aid of an unsealed furnace. In the TGA thermogram, the smooth decrease in weight before and immediately after 470°C is due to the loss of adsorbed moisture and hydrated water. The drastic decrease in weight at 470°C and 710°C corresponds to the decomposition of $Ca(OH)_2$ (dehydration) and $CaCO_3$ (decarboxylation), respectively.

Huijgen et al. (2005) did a study of steel slag, which is a cementitious material used with Portland cement in many mixes. They performed TGA and assumed water was released

between 25-105°C, organic carbon and carbonate associated with magnesium released between 105-500°C, and carbon dioxide from calcium carbonate released above 500°C.

Huntzinger (2006) analyzed cement kiln dust with TGA and assumed that the major mass losses below 500°C were water from hydrated phases and CO_2 was released between 500-800°C.

Chang and Chen (2006) analyzed hydrated cement samples and their test results show that there were three spikes in the derivative curve (DTG curve) related to water loss. The first spike at about 100°C was attributed to the weight loss of the water absorbed in the concrete, the second spike at about 130°C was attributed to the water loss of the interlayer water in the concrete, and the third spike between 425 and 550°C was associated with the mass loss due to the dehydration of Ca(OH)₂. They estimate that mass loss between 550 and 950°C was due to the decomposition of CaCO₃.

Villain and Platrete (2006) performed gammadensity methods, TGA and mass spectroscopy on concrete to determine carbonation profiles. They estimated that CO_2 released between 520 and 620°C are from the C-S-H carbonates or vaterites decomposition.

There was some indication that CO_2 was absorbed in the cement paste in other forms. Cazorla-Amoros et al. (1991) studied CaO-CO₂ interactions by thermogravimetry-differential thermal analysis (TG-DTA), temperature-programmed desorption (TPD), and temperatureprogrammed reaction (TPR). They confirmed that CO_2 chemisorbs on CaO and is restricted to the surface of the particles at T<573K (300°C).

Table 1.1 summarizes the temperature ranges for $Ca(OH)_2$ and $CaCO_3$ decomposition with respect to previous instrumental study analysis.

Author	Experimental Method	Ca(OH) ₂ Decomposition	CaCO ₃ Decomposition	Others
Cole and Kroone (1960)	DTA, TGA and X-ray	500°C	poorly crystallized spike (600-750°C) well crystallized spike (820°C)	There are CO ₂ absorbed in other forms
Taylor et al. (1985 and 1985a)	TGA	400-650°C		
Papadakis et al. (1991)	TGA and X-ray	400-500°C	600-800°C	
Papadakis et al. (1992)	TGA and X-ray	460°C		
Chang et al. (1993)	TGA	470°C	710°C	
Huntzinger (2006)	TGA	500°C	500-800°C	
Chang and Chen (2006)	DTG curve	425-550°C	550-950°C	
Villain and Platrete (2006)	Gammadensity, TGA, and Mass Spectroscopy			C-S-H decomposition (520-620°C)

Table 1.1: Temperature Ranges in Current Studies.

In summary, in most analysis on more traditional cement samples, the lower desorption spike around 150°C was attributed to water absorbed in the cement paste, and the mid-range temperature desorption spike at about 425-550°C was mainly associated with the water from the decomposition of Ca(OH)₂. The dissociation of CaCO₃ was around 700°C in cement paste. There was some indication that CO₂ was absorbed in forms other than CaCO₃.

CHAPTER 2 <u>EXPERIMENTAL METHODS</u>

The purpose of this research was to learn more about concrete chemistry with respect to both CO_2 absorption and new sustainable uses with different environmental exposure under various circumstances. In order to fulfill this objective, there are several basic requirements that need to be met.

- First of all, aged hydrated cement samples need to be made and aged under different environmental conditions to represent different scenarios and different concrete uses, which will be discussed in **Section 2.1**.
- Then, the analysis instrumentation needs to be designed to accomplish the objectives. In this case, a new instrumentation system Temperature Programmed Desorption (TPD) was used other than Thermal Gravimetric Analysis (TGA), which will be discussed in Section 2.2.
- Thirdly, the hydrated cement samples were prepared carefully for the special TPD system to represent the carbon and water content in the corresponding samples and minimize other influences, which will be discussed in **Section 2.3**.
- Fourthly, after all the preparation work has been finished, the samples need to be run through the TPD system and this procedure will be discussed in **Section 2.4**.
- Finally, as soon as CO_2 and H_2O masses were calculated from the amperages by a mass spectrometer, the difference between pre-TPD mass and post-TPD mass was compared with the total mass of CO_2 and H_2O based on the calculation to verify the mass losses, which will be discussed in **Section 2.5**.

2.1 Hydrated Cement Sample Preparation and Aging

The samples for analysis were made by mixing Portland cement with water at a ratio of approximately two moles of water to one mole of calcium (with water to cement "w/c" ratio of approximately 0.4) based on a typical mass concentration of 61% CaO in cement.

These samples were placed in plastic cuvettes at depths of approximately ¹/₄ in (0.635 cm) and aged under various conditions to represent different uses and environmental scenarios (the cuvettes were washed with clean water and dried before the hydrate cement mix was placed inside). The three main paired conditions used were:

- (1) Ambient (A) vs. Oven (O) to represent different temperatures and relative humidity
 (RH) (The ambient environment had 45% RH and room temperature of 20°C on average, while the oven environment had 60% RH and 50°C on average.)
- (2) Covered (C) vs. Open (O) to represent traditional concrete uses versus novel uses such as pervious concrete with substantial exposed surface areas (The covered samples represented cement within walls or slabs not directly exposed to the atmosphere while the open samples represented cement near the edge of walls or in placements that have open structures.)
- (3) Water Drops vs. No Water Drops to represent precipitation or lack of it, or to maintain moisture levels (e.g. soil moisture contributions) (The 'drop' samples had drops of water with average mass of 0.061±0.002 g periodically added to the samples.)

For this experiment, there were eight types of samples based on the above conditions: (1) ambient covered (no extra water drops); (2) ambient open with no extra water drops; (3) ambient open with one extra drop every week; (4) ambient open with two extra water drops every week; (5) oven covered (no extra water drops); (6) oven open with no extra water drops;

(7) oven open with one extra drop every week; (8) oven open with two extra water drops every week.

During the aging period the masses of the samples were also measured on several occasions.

2.2 Instrumentation

As previously mentioned (Section 1.2), Thermal Gravimetric Analysis (TGA), one of the most often used analysis methods on concrete, measures mass loss or gain while the concrete is being heated. Mass can be lost by physical process (e.g. drying) or chemical reactions releasing gaseous composition or even gained if the reaction includes gases in the air absorption and becoming part of the sample. Based on the rate of temperature change and the rate of mass loss at certain temperatures, much information can be gained about the masses of compounds being released and what kind the reactions are. For example, the mass losses around 700°C may be the decomposition of CaCO₃ by releasing CO₂ gas as illustrated in Equation 1.3, and the mass losses around 500°C may be the decomposition of Ca(OH)₂ by releasing water gas.

However, there are many different species in hydrated cement and the chemistry of the concrete as it ages under various environmental conditions is not fully understood, therefore, assumptions have to be made about the predominant species being released at the various temperature ranges. For example, the assumption that water released at temperature ranges around 500°C is predominantly from the decomposition of Ca(OH)₂ rather than water held in the cement paste has to be made when analyzing the hydrated cement samples. In order to differentiate the gases being released if two or more processes or reactions are occurring simultaneously, additional laboratory methods are needed and included downstream which can

analyze the composition of the released gases. The objective of this research was to segregate the two species being released which are CO_2 and H_2O ; thus, either TGA with a gas analyzer or another analysis method needed to be used.

Temperature Programmed Desorption (TPD) and the Inficon Transpector2® gas analyzer were used in this research (Figure 2.1). It is similar to TGA, but the mass losses of the sample during the heating are not recorded. TPD is a process where a sample is heated at a specified rate and a slip stream of the resulting gases 'desorbed' from the sample are analyzed for chemical composition over time. The reactor with a sample was placed in a furnace to be heated with an inert stream of known gases (argon) passing over the sample. Then this bleed stream of these combined inert and released gases from the sample were passed through a mass spectrometer system and the composition of the bleed stream with respect to the elements and compounds of interest were detected based on amperages for various molecular weights. The data for amperages of interested compounds, the total pressure of the bleed stream and the sample temperature were recorded separately every three seconds. This system could only heat up to 800°C. The objective was to determine the amount of CO₂ absorbed by species other than calcite, the water content and hydroxide species formation in early-age hydrated cement. As previously informed in the introduction section, it was confirmed that the decomposition of CaCO₃ was around 700°C and the decomposition of Ca(OH)₂ was 500°C. The hypothesis was that CO₂ would be released slowly under 700°C from other mechanics than the decomposition of calcite.



Figure 2.1: Flow scheme of the Temperature Programmed Desorption (TPD) system (the arrows represent the flow routes of the gases).

The TPD system setup in this research is shown in Figure 2.2. The major components are listed as follows:

- Mass spectroscopy sensor, 300 AMU, EM/FC, High Performance Sensor (H300M); Leybold Inficon; INFICON, Inc.
- (2) Vacuum pump, pressure controller, motor and etc (complete set include power cable), TSU 071E (PMS03 512A), MVP015T (PKT05 058A), TMU071P, TC000; PFEIFFER Vacuum.
- (3) Vacuum pressure gauge, PTR26 002, PKR251, DN40 CF-F; PFEIFFER Vacuum.
- (4) Mass flow controller 840E series, Max 100sccm, Input-output 0-5 VDC, 5 items; Sierra instruments, Inc.
- (5) Split tube furnace; Applied Test System, Inc.
- (6) Data logger for internal reactor temp, HH306 Data logger (K-type); OMEGAETTE ®.
- (7) Temperature controller & indicator (CN77322-C2) 1/16 DIN square Catout-NEMA 12; Omega.



Figure 2.2: Temperature Programmed Desorption (TPD) system setup.

There are several programs and software used to assist in capturing and documenting the signal and data from the analysis. They are listed as follows:

- (1) Dell 521 with Window Microsoft OS and Office; Dell.
- (2) Thermologger version 2.3.0.0 (K-type); OMEGAETTE ® to record temperature data along with time period.
- (3) Temperature control software by Labview, USC, G11X94564; In-House by Shuck to set up initial and final temperature as well as heating rate (temperature ramp rate).
- (4) Tware32 Version 2.84, Single sensor application package; Leybold Inficon (INFICON, Inc.) – to capture and record signal of compounds interested analyzed by mass spectroscopy.

2.3 TPD Specimen Preparation

The samples used in this experiment were taken from a large group of samples which were being aged in various environmental conditions. Over a period of several months, various samples from the groups were removed and prepared for TPD analysis.

In order to fit into the reactor, the cement sample from the cuvette needed to be broken into smaller pieces. There was a concern that the larger samples might also have a water desorption lag due to diffusion through the sample as compared to more finely ground samples. At the same time, there was a concern that preparing finely ground samples would increase contamination during sample preparation from the ambient air. It had previously been found by Haselbach and Ma (2008) that surface exposure of cement to ambient air resulted in fairly rapid carbon dioxide adsorption. In order to determine the relative magnitude of these impacts, two sets of the samples were prepared in pairs with each sample split approximately in half. One half was prepared with the sample in chunks and one half with the sample in coarse powder. The split samples were labeled with a 'C' at the end for the chunk portion and with a 'W' at the end for the powder portion. Each cement sample was simply broken with a sharp implement and the chunks picked out and analyzed together in a separate trial from the remaining powder. The chunks were irregular, typically numbering 10 to 14, with sides usually ranging from 1.5 to 4 mm, with an approximate average volume of about 8.33 mm³. Previous analysis by Haselbach (2009) indicated that there was a small difference between the chunk and coarse powder pairs, but this difference was not significant with respect to the magnitude of the readings in the experiment. If not otherwise noted, all the samples were from then on prepared in the coarse powder form.

When doing the TPD analysis, these samples were took from the cuvettes and placed in the aluminum boats until loaded in prepared reactors for which both pre-TPD and post-TPD masses were taken. The maximum exposing time to ambient environment varied a lot for different samples (see Appendix 3).

2.4 TPD Procedure

2.4.1 Calibration Procedure

Two different types of calibration were explored in this research related to the TPD system. One was for the consistency between the experiments and the other one was for the data analysis to relate the certain amperages to mole ratios.

(a) Calibration for Consistency

The calibration process was required before running the TPD analysis to check the consistency of the TPD system. The purpose to check this consistency was to make sure that the total pressure leakage was linearly related to the amperages of calibrated compounds (see Appendix 1).

Basically, the calibration process follows almost the same procedure with sample running process, which will be discussed later on in Section 2.4.2. The difference is, instead of argon gas flow, the calibration process was using CO_2 30%/He mix gas (The gas was mixed with 30% CO_2 gas and 70% of He gas). For the first calibration process, three kinds of mixed gas flow need to be employed to check the linear relationship of three points, which are 50 sccm, 25 sccm (half CO_2 /He gas and half He gas), and 12.5 sccm (1/4 CO_2 /He gas and 3/4 He gas. For calibration processes later on, only one gas flow rate was needed and the calibration

was fulfilled by varying total pressure for several times. If the total pressure leakage was not in linear relationship with CO₂ amperages, the system was rechecked and recalibrated.

(b) Calibration for Data Analysis

This calibration process was needed to correlate the amperages of certain compounds to associated mole ratios. Correction factors were used to interpret the relationship between the recorded amperages and associated mole ratios of the various gases in the bleed stream for two main reasons: (1) The amperages were recorded by the gas analyzer for different molecular weight ranges which can then be associated with a certain chemical species, for example, a molecular weight range between 17.5 and 18.5 is for water and a range between 43.5 and 44.5 is for CO₂. However, many of the species may be modified or split by the analyzer and then sensed at lower molecular weights. For example, 'OH' (molecular weight 17) is not a typical gaseous species, but in the gas analyzer used, H₂O may be split and contribute to this alternative reading. (2) The amperages also needed to be calibrated for the conversion of amperage readings to actual moles.

The calibration procedure and results for H_2O are in Appendix 2. There are also some correction factors for H_2O from other users, but the values are not consistent. Therefore, published correction factors incorporating all of this to the ratio of H_2O (around 18) to Ar (around 40) by 1.33 and CO_2 (around 44) to Ar (around 40) by 1.02 (INFICON 2008) were used in this research.

2.4.2 Sample Running Procedure

There were two different setups for this experiment based on two different types of reactors, which were pyrex reactor and quartz reactor shown in Figure 2.3. The pyrex reactor (Figure 2.3a) was used for the samples which were heated only up to 550°C because in temperatures

higher than 550°C, the glass would melt, the reactor would be broken, and the mass spectrometer would be damaged. For the samples which were heated up to 700°C the quartz reactor (Figure 2.3b) was used.





Note: For the quartz reactor, the quartz wool was put in the middle of the reactor which was functioning as the frit to hold up the samples.

Before running the TPD analysis, the samples need to be loaded in the corresponding reactor, either pyrex or quartz reactor. After loading the samples, the reactor was fit into the furnace, the thermocouple was placed in position, the argon gas flush system was set, the data collection software both for mass spectrometer and temperature were ready, and the experimental analysis was ready to run. These processes are explained in detail as follows:

- (1) Loading Samples
 - a. Load the cement sample in either a clean pyrex reactor for the ones that need to go to 550° C or a quartz tube reactor for the ones that need to go to 700° C. Take the mass of the reactor both before and after loading the sample. The reactors were covered with wax papers for both ends to minimize the contamination by CO₂ from ambient air.

- b. Fix the reactor into the furnace in the right position using fittings. Make sure to tight on the upper and lower nuts and o-rings. Put quartz wool in the furnace at both top and bottom for insulation.
- c. Put the thermocouple into the middle of the sample. The thermocouple is connected to the temperature controlling device.
- (2) Setting Argon Gas Flow
 - a. Select a predetermined flow rate of a set gas composition (mixed gas mixture), which was argon gas following through the reactor at 50 sccm.
 - b. Turn on the mass flow rate controller. Then set the number to the desired flow rate.
 - c. Switch the gas valve and make the argon gas flow through the furnace and check the gas flow to meet the desired flow rate.
 - d. Check the leakage. Check the flow rate with the gas flow monitor (GFM) and adjust to 50 sccm. Then switch the three-way valve to other way and make sure the valve under the furnace pointing away from the mass spectrometer machine to check the leakage for the furnace with GFM. Make sure the flow rate consistent. If not, there is some leakage going on around connection between the reactor and the furnace.
- (3) Preparing Tware 32 Program for Mass Spectroscopy

Before running the samples, a recipe including sensor name and recipe name needs to be selected and edited in the Tware32 program. A recipe is a listing of the interested compounds itemized by molecular weights. First, the trend display masses need to be chosen based on the interested compounds, i.e., 18 for H₂O, 28 for CO or N₂, 32 for O₂, 40 for Ar, 44 for CO₂. Choose the start mass to be 1 and end mass to be 50 (five times

more than the higher mass during the experiment). Next, set the interval between mass spectroscopy scans to 3 seconds and save the recipe to be used later on.

When choosing and running the recipe, three graphs would be shown in the Tware32 program (Figure 2.4). The top one is the plot of total pressure versus time; the middle one is the plot of partial pressure of each interested element with different masses versus time, which can be shown in the form of either 'Torr' or 'Amps'; the bottom one is the plot of all the element masses as a function of real time scan and was updated every three seconds. Both the pressure scale and time scale can be adjusted for better viewing. For example, the time scale can be set either for five minutes to compare a portion of the different desorption curves or for two hours to view the overall trends for the desorption curves.



Figure 2.4: Output of Tware32 for a cement sample.
After starting the program, the signals would decrease and eventually settle down to a stable value. The signal during this time period is the measurement of existing compounds either in the furnace or in mass spectroscopy chamber. The stabilized signal is basically the background for all the interested elements. The data can be collected from then on and the total pressure should always be less than 5×10^{-6} torr. This was a requirement as determined by other users of the system to prevent the TPD system from breaking down.

- (4) Starting Temperature Program
 - a. Thermologger Software

Turn on the temperature data logger and set the rate as three seconds which is the same as recording time of mass spectroscopy. To record the temperature data, click on the play button and it will record the internal temperature in the sample.

b. Controller PV Read Software

The set point in the Controller PV Read Software always need to be set 60-70°C lower than the maximum temperature required by the experiment. Therefore, for samples need to be heated to 550°C, the set point was 470°C; for samples need to be heated to 700°C, the set point was 620°C. The best range for the ramp rate for the furnace is 2-50°C/min, and it was 10°C/min for this experiment.

(5) Running Experiments

When the Tware32 software shows stable signals of total and partial pressure, the experiment is ready to run. Start the programs, the Thermologger and Controller PV Read, and switch the power on for the furnace in order. The Tware32 would show the signal for interested gases of mass spectroscopy analysis based on 3-second increments.

During the whole experiment-running process, keep checking the total pressure to make sure that they are stabilized around 1×10^{-6} torr. And the all the amperages need to be normalized later on.

(6) Stopping Experiment

As soon as the experiment is completed, the system needs to be stopped and cooled down. It is important to cool the furnace down in order to prevent injury and damages. In the end, make sure all the programs which are listed as follows have been turned off:

- a. Stopping the process and cool down
 - In Tware 32 software, click the start/stop button to stop recording of mass spectrum information.
 - 2) In Thermologger software, click stop button.
 - 3) Close leak valve slowly until the total pressure get less than 1×10^{-9} torr. Record the vacuum pressure until it does not got lower. This is a system requirement that all the users of this system did to double check and see if there was any vacuum leaks on pressure.
 - For the Controller PV Read, shut down the system and turn off the heat switch. Click time stop button.
 - 5) Open furnace carefully.
 - 6) Use fan to cool down to room temperature. This is necessary for the safety and also for the next sample analysis because all the samples started from room temperature.
- b. Saving data
 - 7) Thermologger: Save the all temperature data along with time.

 Tware 32: The signal can be saved both as a graph and as a text file which was used later on for analysis.

2.5 TPD Mass Change Verification

In principle, the mass differences between the pre-TPD sample mass and post-TPD sample mass should be equal to the total mass of the gases released during the experiments. In this TPD analysis, it was assumed that the gases released under 550°C would mainly be water and carbon dioxide and other gases can be ignored since the masses would be so small compared to the masses of water and carbon dioxide.

In order to verify this assumption, the percent difference of mass losses between the weighed masses (mass difference between pre-TPD mass and post-TPD mass) and calculated masses (summed up mass losses of H_2O and CO_2 at this temperature ranges based on the calculations by molecular weights) need to be calculated. If the percent difference is within the range of $\pm 10\%$, then the assumption would be valid for this analysis.

CHAPTER 3 CARBON DIOXIDE ABSORPTION POTENTIAL IN CONCRETE

As previously mentioned, based on the chemistry of hydrated concrete exposed to carbon dioxide under certain pH conditions and also complexation chemistry, there is a potential for carbon dioxide absorption in intermediate absorbed/dissolved forms in the cement paste in addition to the final carbonation products, i.e. calcium carbonate. One of the objectives of this research was to show that there can indeed be significant amounts of carbon dioxide absorbed in hydrated cement pastes, which will be released at lower temperature ranges than where calcium carbonate dissociates. It is important for understanding the overall carbon footprint of concrete and may help in developing methods to accelerate carbon dioxide absorption in concrete and remediate the global warming potential issues with respect to carbon dioxide.

This chapter focuses on mass balances around carbon dioxide released from various samples of TPD analysis for the temperature ranges of $0-550^{\circ}$ C. CO₂ released in this lower temperature ranges represents carbon absorbed in certain forms other than the solid calcium carbonate (calcite).

This chapter covers the following sections:

- Section 3.1, Water and Carbon Dioxide Amperages from TPD Analysis, will demonstrate the water and carbon dioxide desorption curves as temperature goes up to 550°C.
- Data Acquisition, **Section 3.2**, will discuss how to convert the amperages of water and carbon dioxide recorded during the TPD analysis to corresponding mass losses at lower temperature ranges.
- Section 3.3, Results, will show how to interpret the data based on the calculations from Section 3.2 and how to relate the CO₂ released masses to percent carbon absorption in the cement paste.

- Discussions, **Section 3.4**, include the interpreted results, the significance of this carbon absorption at lower temperature ranges and the impact on the chemistry of hydrated cement paste.

3.1 Water and Carbon Dioxide Amperages from TPD Analysis

The following data files were generated every time the TPD analysis was carried out: amperage files from the mass spectrometer and temperature files from the thermocouple. The amperages and temperatures from the two data files were synchronized based on the same time series. The recorded amperages in the synchronized files were first normalized based on a constant total pressure of 1×10^{-6} torr in the bleed stream (see Section 3.2). Figures 3.1 and 3.2 give typical depictions of water and carbon dioxide desorption from the TPD analysis for the amperages recorded over the temperature ranges for molecular weights of 18 and 44 respectively. The left axis represents the amperages as normalized for leak rate pressure for the mass range around 18, which represents water. The right axis is the summed amperages as normalized for leak rate pressure around 44, which represents CO₂. (The normalized water and carbon dioxide desorption curves for the rest samples in this group are in Appendix 3.)



Figure 3.1: Water and CO_2 desorption curves for sample AOX31PW. (The water curve has the left spike with values on the left vertical axis, while the CO_2 curve has the right spike with values on the right vertical axis.)



Figure 3.2: Water and CO_2 desorption curves for sample AC7W. (The water curve has the large left spike and the smaller right spike with values on the left vertical axis, while the CO_2 curve has the right spike with values on the right vertical axis.)

In Figures 3.1 and 3.2, the dashed lines are the water amperages over the temperature range of the thermal desorption tests performed. These lines show significant water desorption under 200°C, which based on previous studies is expected to be the release of free and absorbed water in the hydrated cement paste. A second water spike after 400°C is the indicative of the dissociation of calcium hydroxide. In most of the trials for open samples, there was only the large water spike prior to reaching 200°C as shown in Figure 3.1 while both water spikes were developed in most of the covered samples as shown in Figure 3.2. These water-related issues will be discussed in **Chapter 4**.

The large spike in the carbon dioxide curve developing prior to 500° C indicates that species were being desorbed that are not in the solid calcium carbonate form. The amounts of this portion of CO₂ need to be determined for further calculation of the percent carbon absorption by forms other than calcite.

3.2 Data Acquisition

In this experiment, the system used Tware32 to collect amperages data over time from mass spectrometer and Thermologger to collect temperature data over time from the thermocouple. The recorded amperages from the TPD analysis were normalized based on total pressure in the bleed stream. The bleed stream pressure varied by as much as $\pm 50\%$ during the course of the experiments and based on the Ideal Gas Law, at constant temperature and volume, the pressure is proportional to the number of moles of a gas. Therefore multiplying the amperage by the ratio of the normalized pressure of 1×10^{-6} torr to the actual total bleed stream pressure would give relative mole ratios for the various slip stream gases based on a known argon flow.

Then these normalized amperages were added over the duration of each analysis to give an integrated total of amperages for each of the three molecular weight ranges: 17.5-18.5 for H_2O , 39.5-40.5 for Ar, and 43.5-44.5 for CO_2 . The molar percents of water and carbon dioxide in the bleed stream with respect to argon were determined by the ratios of the summed amperages for water and CO_2 to argon and appropriate correction factors, respectively. Then total moles for each compound were determined by multiplying by the constant argon flow rate through the reactor over the duration, and calculating the masses based on the molecular weights. A summary of these steps and the equations used are as follows:

- (1) Synchronize the amperages data files to the corresponding temperature data files based on the same time period.
- (2) Convert all the data files to 30 seconds increments instead of 3 seconds increments, in order to make the data calculation easy and efficient.
- (3) Normalize the amperages for all molecular weights to a constant total pressure of 1×10^{-6} torr in the bleed stream by dividing the amperages by the actual bleed stream pressure then multiplying by 1×10^{-6} torr.
- (4) Add all the amperages over the duration of each experiment around certain molecular weight: 17.5-18.5 for H₂O, 39.5-40.5 for Ar, and 43.5-44.5 for CO₂ to account for equipment sensing fluctuations over these ranges.
- (5) Correct for background levels of H₂O and CO₂, that is, the lowest normalized amperage for the 17.5-18.5 and 43.5-44.5 molecular weight range during the experiment. This portion of H₂O and CO₂ is the background water and CO₂ gas contained in the inert gas mixture or from other water forms or air leaked into the system. It was based on the

assumption that no H_2O and CO_2 desorption would occur when the sample was not being heating.

- (6) Apply the correction factors CF_{H2O} 1.33 for H₂O and CF_{CO2} 1.02 for CO₂: There are other species representing H₂O, CO₂ and argon as measured in amperages, for example, 20 is another form of argon and OH (17g/mol) may be water breakdown. The analyzer also senses the various molecular weights differently. So amperages of H₂O and CO₂ to argon need to be related, respectively. There is a published factor incorporating all of this to the ratio of H₂O around 18 to Ar around 40 by 1.33 and CO₂ around 44 to Ar around 40 by 1.02 (INFICON 2008).
- (7) Use ratios of the summed amperages for water to argon and CO_2 to argon to determine the molar fraction of water and CO_2 in the bleed stream with respect to argon using appropriate correction factors as in Equations 3.1 and 3.2.

$$H_2O \ mole \ ratio = \frac{molesH_2O}{molesAr} = CF_{H_2O} \cdot \frac{ampsH_2O}{ampsAr}$$
(3.1)

$$CO_2 \text{ mole ratio} = \frac{molesCO_2}{molesAr} = CF_{CO2} \cdot \frac{ampsCO_2}{ampsAr}$$
 (3.2)

(8) Use Equations 3.3 and 3.4 to calculate the mass losses of H_2O (L_{H2O}) and CO_2 (L_{CO2}) in grams over a certain time or temperature range:

$$\sum_{\Delta t} \left[\left(\frac{molesH_2O}{molesAr} \right) \cdot \left(\frac{50ccAr}{\min} \right) \cdot \left(\frac{1molAr}{22400ccAr} \right) \cdot \left(\frac{18gH_2O}{molesH_2O} \right) \right] = L_{H_2O}$$
(3.3)

$$\sum_{\Delta t} \left[\left(\frac{molesCO_2}{molesAr} \right) \cdot \left(\frac{50ccAr}{\min} \right) \cdot \left(\frac{1molAr}{22400ccAr} \right) \cdot \left(\frac{44gCO_2}{molesCO_2} \right) \right] = L_{CO_2}$$
(3.4)

(9) Double check mass losses to see if the assumptions are reasonable (see Section 2.5).Express the difference in percent as shown in Equation 3.5:

$$\% Difference = \frac{(m_{TPD-pre} - m_{TPD-post}) - (L_{H_2O} + L_{CO_2})}{(m_{TPD-pre} - m_{TPD-post})} \times 100\%$$
(3.5)

3.3 Results

This section shows how to develop a way of estimating the percent carbon absorption – Isohydration Diagram (Section 3.3.1), the results of estimated carbon absorption using this curve (Section 3.3.2), and the repeatability of the experiments (section 3.3.3).

3.3.1 Isohydration Curve

One of the difficulties with analyzing the data is that there is no way to regulate the amounts of carbon dioxide and water that are absorbed or desorbed at all times. The masses of the cement and water used in the initial preparation of the samples are known, so based on the typical composition of cement it is initially possible to determine the moles of calcium in any sample. However, since both water and carbon dioxide absorption and desorption are taking place at the same time and are responsible for a sample's mass change, it is not possible to determine the mass percent of calcium in any sample during the duration of the experiment. Since it is necessary to know the amount of calcium in a sample in order to determine the molar ratio of carbon to calcium (percent carbon absorption), a way of estimating the percent carbon absorbed needed to be developed.

The samples after the TPD experiments are most closely resemble samples where there is little or no water in the sample since they have been heated well past the dissociation temperature of Ca(OH)₂. In order to develop a reasonable approach to estimate the percent carbon absorbed in a hydrated cement sample, the following example of sample AOX33PWD is used. Sample AOX33PWD is an open sample which was aged for 3.6 months in the ambient environment with two extra drops of water every week (A drop of water is approximately 0.061 g). The post-TPD mass of this particular sample was 0.218 g, and the CO₂ released in the lower temperature range ($<550^{\circ}$ C) was 0.00454 g. First, let us assuming that there was no CO₂ and no H₂O left after the TPD analysis, then the percent CO₂ absorption would be:

$$\% Carb = \frac{n_{CO_2}}{n_{CaO}} \times 100\% = \frac{0.00454g / (44g / mol)}{(0.218g \times 0.61) / (56g / mol)} \times 100\% = 4.342\%$$

where,

- %Carb is percent CO₂ absorption with respect to CaO;
- n_{CO2} is the moles of CO₂ released after the TPD analysis at lower temperature ranges;
- n_{CaO} is the moles of CaO in the cement samples after TPD analysis at lower temperature ranges.

If there was some CO_2 left in the sample after the TPD analysis, the percent CO_2 absorption would be different. The results are listed in Table 3.1, assuming no additional carbonation and no H₂O in the sample.

Percent CO ₂ Left (%)	Post-TPD Mass (g)	CO ₂ Released (g)	Percent CO ₂ Absorption (%)
0			4.342
10			4.787
20	0.218		5.233
30			5.681
40		0.00454	6.131
50		0.00+3+	6.582
60			7.036
70			7.491
80			7.949
90			8.408

Table 3.1: Different Percent CO₂ Absorption Based on Different Percent CO₂ Left after the TPD Analysis at Lower Temperature Ranges (<550°C).

However, there could still be some water in the samples in other hydrated forms. So in order to predict if the water is important for determining the ratio of carbon dioxide to calcium in a post-TPD sample a series of 'isohydration' curves have been developed (Haselbach, 2009), which is depicted in Figure 3.3. The curves represent heated sample masses of carbon dioxide lost in the TPD test per predicted percent carbon dioxide absorption with various percentages of water still remaining in the samples. All numbers in Figure 3.3 are based on the assumptions that there is no CO_2 left in the samples. This is a very conservative assumption since some CO_2 is expected to remain as $CaCO_3$. As can be seen from Figure 3.3, although the water left in the sample does change the percentages, for low water content, which is a reasonable assumption, the water masses can be ignored.



Figure 3.3: Isohydration Diagram for cement with 61 mass percent CaO. (100% Water represents one mole water per one mole CaO. Percent Carbon Absorption represents the molar ratio of Carbon Dioxide per mole CaO, in percent, assuming no additional carbonation in the sample.)

Interpretating the above curve will show that a TPD experiment with the mass loss due to carbon dioxide measured at 4.5% gives, at a minimum, an absorption ratio of 10% based on moles carbon to moles calcium (absorption ratio reads even higher if there are water species remaining in the sample). In cases where carbonation is also extensive and much of the post TPD mass is from calcite, this percent would be even higher. In summary, the values read off the Isohydration Diagrams would give a value for the minimum estimated value of percent carbon absorption in a form other than the calcium carbonate solid species (calcite) for samples where there is no carbon remaining in the samples. In reality, some carbonation is expected to occur and therefore the estimates of carbon absorption in these experiments are very low.

3.3.2 Estimated Percent Carbon Absorption at Lower Temperature Ranges

Tables 3.2 and 3.3 list the results of calculated mass losses based on the molecular weights for water and carbon dioxide at lower temperature ranges (lower than 550°C) from Haselbach (2009).

Sample Age (months)	Sample	Number of Water Drops Added Pre-TPD	After TPD Mass (g)**	Mass Loss H ₂ O from TPD (g)	Mass Loss CO ₂ from TPD (g)	% H ₂ O MassLoss After TPD*	% CO ₂ MassLoss After TPD*	Minimum Molar % Carbon Absorbed from 0% Isohydration Curve	Avg. % Mass H ₂ O Loss After TPD* Powder Samples	Avg. Minimum Molar % Carbon Absorption Powder Samples
2.8	AC7C	2	0.204	.0125	.0062	6.1	3.1	6.8		
2.8	AC7W	2	0.108	.0087	.0046	8.1	4.3	9.4	7 /	10.0
2.8	AC8C	6	0.192	.0124	.0075	6.4	3.9	8.5	/.+	
2.8	AC8W	6	0.148	.0099	.0070	6.7	4.8	10.5		
2.8	AO8C	4	0.244	.0132	.0060	5.4	2.5	5.5		
2.8	AO8W	4	0.266	.0143	.0073	5.4	2.8	6.1	60	62
2.8	AO9C	10	0.226	.0151	.0062	6.7	2.7	5.9	0.0	0.2
2.8	AO9W	10	0.232	.0151	.0067	6.5	2.9	6.3		
1.0	ACXX7PC	4	0.184	.0146	.0037	8.0	2.0	4.4		
1.0	ACXX7PW	4	0.226	.0178	.0041	7.9	1.8	3.9	87	5 1
1.0	ACXX9PC	10	0.242	.0217	.0053	9.0	2.2	4.8	0.7	J.1
1.0	ACXX9PW	10	0.206	.0193	.0059	9.4	2.9	6.3		
1.0	AOX31PC	6	0.216	.0844	.0054	3.9	2.5	5.5		
1.0	AOX31PW	6	0.214	.0959	.0057	4.5	2.7	5.9	18	62
1.0	AOX36PC	10	0.240	.0113	.0061	4.7	2.5	5.5	4.0	0.2
1.0	AOX36PW	10	0.226	.0114	.0067	5.0	3.0	6.6		

Table 3.2: Results from the TPD Experiments for Samples Heated to 550°C with Assumed Low Levels of Carbonation (Haselbach, 2009).

**Masses are not precise due to precision of scale.

Table 3.3: Results from the TPD Experiments for Samples Heated to 550°C with Assumed Higher Levels of Carbonation (Samples were left open (O) in an oven (O) with ~ 60% relative humidity) (Haselbach, 2009).

Sample Age (months)	Sample	Number of Water Drops Added Pre-TPD	After TPD Mass (g)**	Mass Loss H ₂ O from TPD (g)	Mass Loss CO ₂ from TPD (g)	% H ₂ O Loss After TPD*	% CO ₂ Loss After TPD*	Minimum % Carbon Absorbed from 0% Isohydration Curve	Avg. % H ₂ O Mass Loss After TPD*	Avg. Minimum Molar % Carbon Absorption
4.1	OO18WD	8	0.238	.0197	.0060	8.3	2.5	5.5		
4.1	OO19WD	9	0.240	.0185	.0052	7.7	2.2	4.8	80	5.0
4.1	OO20WD	10	0.226	.0173	.0048	7.7	2.1	4.6	0.0	5.0
4.1	OO21WD	14	0.238	.0195	.0055	8.2	2.3	5.0		
4.1	OO18WN	0	0.232	.0166	.0048	7.1	2.1	4.6		
4.1	OO19WN	0	0.206	.0144	.0043	7.0	2.1	4.6	6.6	13
4.1	OO20WN	0	0.246	.0159	.0042	6.5	1.7	3.7	0.0	4.5
4.1	OO21WN	0	0.246	.0143	.0048	5.8	1.9	4.2		
2.3	OOX31PWD	8	0.220	.0122	.0052	5.5	2.4	5.2		
2.3	OOX32PWD	10	0.214	.0124	.0050	5.8	2.4	5.1	5.0	5 1
2.3	OOX33PWD	10	0.220	.0131	.0050	6.0	2.3	4.9	5.7	5.1
2.3	OOX34PWD	14	0.226	.0146	.0054	6.4	2.4	5.2		
2.3	OOX31PWN	0	0.232	.0113	.0051	4.9	2.2	4.8		
2.3	OOX32PWN	0	0.210	.0104	.0046	5.0	2.2	4.8	5.0	46
2.3	OOX33PWN	0	0.208	.0105	.0042	5.1	2.0	4.4	5.0	1.0
2.3	OOX34PWN	0	0.218	.0111	.0045	5.1	2.1	4.5		

**Masses are not precise due to precision of scale.

Note: The following molecular weight ranges were used for the calculation: 17.5-19 for H_2O , 39.5-41 for Ar, and 43.5-45 for CO_2 .

Tables 3.4 and 3.5 list the results of mass losses for H_2O and CO_2 of the rest of the TPD experiments which had been heated up to 550°C and 700°C, respectively. Note that the mass losses for H_2O and CO_2 might have been corrected for slightly different background amperages using a conservative correction approach. This conservative correction was based on the assumption that the H_2O and CO_2 gases released prior to heating in the furnace were the background gases.

Sample Ages (Months)	Sample Name	Number of Water Drops Added Pre-TPD	Post- TPD Mass (g)	L _{H2O} (g)	L _{CO2} (g)	% H ₂ O Loss After TPD (%)*	% CO ₂ Loss After TPD (%)*	Min. % Carbon Absorption from 0% Isohydration Curve (%)	Avg. %H ₂ O Mass Loss After TPD (%)	Avg. Min. Molar %Carbon Absorption (%)	% Difference (%)
5.0	OO27D	1	0.246	0.0280	0.0035	11.4	1.4	3.1	10.5	3.6	-4.7
5.0	OO28D	1	0.244	0.0234	0.0045	9.6	1.9	4.0	10.5		0.5
5.0	OO27N	0	0.234	0.0184	0.0030	7.9	1.3	2.8	61	20	-7.0
5.0	OO28N	0	0.234	0.0101	0.0032	4.3	1.3	2.9	0.1	2.9	5.0
3.6	AOX32PWD	1	0.216	0.0127	0.0048	5.9	2.2	4.9			3.1
3.6	AOX33PWD	1	0.218	0.0129	0.0045	5.9	2.1	4.6	60	46	3.2
3.6	AOX34PWD	1	0.222	0.0133	0.0046	6.0	2.1	4.5	0.0	4.0	0.9
3.6	AOX35PWD	1	0.216	0.0132	0.0044	6.1	2.0	4.5			2.0
3.6	AOX32PWN	0	0.22	0.0142	0.0040	6.4	1.8	4.0			-0.9
3.6	AOX33PWN	0	0.226	0.0127	0.0040	5.6	1.8	3.8	63	<i>A</i> 1	-3.9
3.6	AOX34PWN	0	0.214	0.0135	0.0041	6.3	1.9	4.2	0.5	4.1	2.2
3.6	AOX35PWN	0	0.212	0.0142	0.0041	6.7	1.9	4.2			-1.6

Table 3.4: Results from the TPD Experiments for Samples Heated to 550°C.

Note: The following molecular weight ranges were used for the calculation of the first four samples: 17.5-19 for H₂O, 39.5-41 for Ar, and 43.5-45 for CO₂.

Sample Ages (Months)	Sample Name	Number of Water Drops Added Pre-TPD	Post- TPD Mass (g)	L _{H2O} (g)	L _{CO2} (g)	% H ₂ O Loss After TPD (%)	% CO ₂ Loss After TPD (%)	Min. % Carbon Absorption from 0% Isohydration Curve (%)	Avg. %H ₂ O Mass Loss After TPD (%)	Avg. Min. Molar %Carbon Absorption (%)	% Difference (%)
5.6	AOX37Pa	0	0.252	0.015	0.030	6.1	11.8	28.0			-2.3
5.6	AOX37Pb	0	0.292	0.018	0.053	6.3	18.0	45.9	60	30.1	-36.2
5.6	AOX38Pa	0	0.252	0.013	0.026	5.2	10.5	24.5	0.0		1.2
5.6	AOX38Pb	0	0.246	0.016	0.023	6.5	9.5	21.9			-3.5
5.6	ACXX6Pa	0	0.274	0.023	0.035	8.3	12.9	30.9			-7.9
5.6	ACXX6Pb	0	0.206	0.025	0.035	12.0	16.8	42.1	82	33.2	-13.8
5.6	ACXX8Pa	0	0.230	0.014	0.033	6.0	14.5	35.4	0.2	55.2	-2.5
5.6	ACXX8Pb	0	0.268	0.017	0.028	6.5	10.5	24.5			-3.4
5.6	OOX36Pa	0	0.260	0.011	0.021	4.1	8.0	18.2			7.5
5.6	OOX36Pb	0	0.278	0.010	0.023	3.7	8.1	18.5	3.8	23.4	9.2
5.6	OOX38Pa	0	0.224	0.008	0.031	3.5	13.8	33.5			-29.7
5.6	OCXX6Pa	0	0.216	0.020	0.032	9.1	14.8	36.3			-17.4
5.6	OCXX6Pb	0	0.238	0.019	0.039	8.1	16.4	41.0	82	37.6	-7.8
5.6	OCXX8Pa	0	0.206	0.017	0.028	8.2	13.4	32.3	0.2	57.0	-1.4
5.6	OCXX8Pb	0	0.216	0.016	0.035	7.2	16.3	40.7			-5.7

Table 3.5: Results from the TPD Experiments for Samples Heated to 700°C.

The values in the column of Percent CO_2 Loss After TPD in Tables 3.2, 3.3 and 3.4 indicate that the percent carbon dioxide mass loss in all these samples are not more than 10%, therefore, a small portion of the Isohydation Diagram could be used to determine the percent carbon absorption instead of the whole diagram. For the samples in Table 3.5, the percent carbon absorption was estimated from the original Isohydation Diagram (Figure 3.3).

Figure 3.4 is a depiction of the lower portion of the Isohydration Diagram and gives an approximate linear relationship for carbon absorption under 10% of the stoichiometric mass

percent carbon dioxide. Only the linear regression line for 0% water was generated based on the assumption that there was no H_2O left in the samples after the TPD analysis.



Figure 3.4: Isohydration Diagram for cement with 61 mass percent CaO lower portion. (100% Water represents one mole water per one mole CaO. Percent Carbon Absorption represents the molar ratio of carbon dioxide 'loosely' held per mole CaO, in percent, assuming no additional carbonation in the sample.)

Based on the above diagram, the last column in Tables 3.2 and 3.3 and the second to the last column in Table 3.4 give the minimum percentage estimated for the amounts of absorbed carbon dioxide which would be released prior to heating up to 550° C in the power form of the samples. The second to the last column in Table 3.5 give the percent carbon absorption which would be released prior to heating up to 700° C in the powder forms.

The last column in Tables 3.4 and 3.5 give the percent difference between the mass losses during the TPD analysis and the summed up masses of water and carbon dioxide at lower temperature ranges.

3.3.3 Repeatability of the Experiments

Repeatability is the variation of outcomes of an experiment carried out in the same conditions, e.g. by the same operator, in the same laboratory. For example, repeatability of measurements of precise mechanical scales is the variation of weight values reported for a given constant mass by the same person, in conditions with the same temperature and humidity. For continuous outcome variables, repeatability may be quantified via such measures as "repeatability standard deviation " or "repeatability variance ".

In this case, the repeatability would be the variation of the percent water loss and percent carbon dioxide loss of the TPD analysis. In order to determine the repeatability of the experiments, the four samples in Table 3.3 listed from OO18WN through OO21WN were all treated identically, so as were the four samples in Table 3.3 identified as OOX31PWN through OOX34PWN. Table 3.5 lists the standard deviations for percent water losses and percent carbon dioxide losses for these two sets of sample analysis, which shows the good reliability of the test method.

9	6 H ₂ C) Loss (%)		% CO ₂ Loss (%)					
Set 1		Set 2	Set 1		Set 2				
OO18WN	7.1	OOX31PWN	4.9	OO18WN	2.1	OOX31PWN	2.2		
OO19WN	7.0	OOX32PWN	5.0	OO19WN	2.1	OOX32PWN	2.2		
OO20WN	6.5	OOX33PWN	5.1	OO20WN	1.7	OOX33PWN	2.0		
OO21WN	5.8	OOX34PWN	5.1	OO21WN	1.9	OOX34PWN	2.1		
Average	6.6		5.0		2.0		2.1		
Stdev	0.6		0.1		0.2		0.1		

Table 3.6: Standard Deviation of Two Sets of Samples with Final Temperature of 550°C to Test Repeatability of TPD Analysis (Samples from Table 3.3).

3.4 Discussions

3.4.1 Impact of Sample Size on Desorption Rate

Two important considerations in the experimental setup were how the rate of diffusion through the sample of either of the compounds of interest (water and carbon dioxide) might impact the measured desorption rate and how increased exposure during the sample preparation prior to the TPD analysis might alter the results.

As discussed by Haselbach (2009), there was a slight difference in water desorption rates between the samples prepared for the TPD analysis in chunk (C) or coarse powder form (W). The ambient open and ambient covered samples in Table 3.2 provide the information on how the sample size impacts the desorption rate. On average, the chunk trials had a slightly lower desorption rate for both H_2O and CO_2 , with greater difference for the CO_2 since the larger molecular.

However, since the desorption rates were well within the same order of magnitude, even with the large size differences between chunk and coarse powder, it could be assumed, that in the powder form, as prepared, the diffusion rate during the TPD analysis and the exposure to the ambient environment during preparation do not significantly impact the desorption rate as measured under the experimental conditions used. With this determination, the assumption can now be made that the TPD experiments as performed with the coarse powder samples give adequate representations of the chemical desorption rate of water and CO_2 from the samples. Therefore, all the tests and calculations in this research were performed on powder samples as described in Section 2.3.

3.4.2 Sample Mass Variations While Aging

During the aging period some of the samples were covered after initial preparation, while some were left open in the air. It was noted during the aging period that there were initially significant mass losses in the open hydrated cement samples, which would indicate water evaporation under certain environmental conditions, but there were also initial mass losses in both the ambient and oven covered hydrated cement samples, which were much less than that of open samples counterparts. This phenomenon is depicted in Figure 3.5.



Figure 3.5: Comparison of normalized mass of ¹/₄ in covered and open samples for both ambient and oven (Note: ACP represents the ambient covered cement samples; AOP (No Drops) represents the ambient open samples with no extra water drops; OCP represents oven covered cement samples; OOP (No Drops) represents the oven open samples with no extra water drops. The dash line means the samples have been placed to another place with different environments from before).

All the masses were normalized to the initial masses and averaged over the similar samples under the same aging condition in order to be more representative. As can be seen in Figure 3.5, all the four types of cement samples lost significant amounts of mass immediately after initial preparation and the normalized masses for open samples (0.74) were lower than those for the covered samples (0.80). Therefore, air exchange could occur in all the samples,

but more readily in the open samples. This was not of concern in the experimental setup as traditional concrete placements would also have some potential for air exchange as concrete is a porous medium.

3.4.3 The Mass Change Verification Analysis

In the TPD analysis for this research, it was assumed that the compounds released over the duration of the experiments were mainly H_2O and CO_2 gases and the amounts of other gases were negligible. In order to verify this assumption, the percent difference between weighed mass losses and calculated mass changes were derived and compared as listed in the last column in Tables 3.4 and 3.5. The percent differences for samples in Tables 3.2 and 3.3 were not considered in this analysis due to the precision of the scale.

As can be seen, the percent differences for the samples in Table 3.4 which were heated to 550° C were in the range of $\pm 10\%$, which indicates that the assumptions made before about the mass losses were reasonable considering the variability and deviation of the experiments on cement samples. However, for the samples in Table 3.5 which were heated to 700° C, the percent differences varied from -36.2% to 9.2% with an average value of -10.3%, which means the calculated mass losses were 10% more than the weighed mass changes. This was conflicting with the assumptions on mass losses and there might be some reasons for this: (1) the TPD system becomes less accurate and sensitive after passing 550°C, and most of the users were applying it under 500°C; (2) as the heating temperature goes up, more compounds would tend to decompose and be released from the samples, which would make the differences larger; (3) the correction factors for H₂O and CO₂ which contributed significantly to the calculated mass losses might not be precise and suitable for this experiment on cement samples; (4) the cuvettes used as containers might have some carbon or organic carbon that might have

transferred in the cement samples. More future work on the cement mixture and calibration process of the correction factors for the TPD system needs to be completed to resolve this problem and modify the experimental setup.

3.4.4 Percent Carbon Absorption

Based on the percentage of carbon dioxide released during the TPD analysis at lower temperature ranges and the Isohydration Diagram, the percentage of carbon absorption can be estimated assuming that there is no carbon left in the samples after the TPD analysis, which is listed in Tables 3.2, 3.3, 3.4 and 3.5.

The last column in Table 3.2 gives the minimum percentage estimated for the amounts of carbon dioxide absorbed which would be released prior to heating up to 550°C in the mass spectrometer in the powder-form samples. These average percentages of carbon absorption range from 5 to 10%, which means at least 5 to 10% of carbon dioxide is absorbed in the samples by other forms than solid calcium carbonate. The samples which received more water drops during the specimen preparation process prior to the TPD tests consistently showed at least 10% higher percent carbon dioxide absorption than the ones which did not receive extra water drops. This might have been the results that the carbon can be further absorbed into the samples in the presence of extra moisture. There is also possibility that the extra water may prohibit the carbon from releasing to the air or reaching the equilibrium under the ambient environment condition.

The samples in Table 3.3 were all aged open in the oven with a relative humidity of approximately 60%, which is considered to be a relative humidity level under which conditions are favorable for carbonation. Therefore, it is assumed that these samples may have already experienced some carbonation. If some carbonation has occurred, then the actual percent

carbon absorption of species other than calcite would be higher than the percentages in the last column in Table 3.3. As previously mentioned, until further determinations of the extent of carbonation are also determined, these percentages in the last column are the minimum calculated based on the assumption that there is no carbonation in the samples. Even though that is true, the percentages indicate that there is consistently a significant amount of carbon dioxide absorption in the samples. The samples in Table 3.3 were prepared in pairs, with half of each specimen treated with additional water drops in open, ambient conditions prior to the TPD and the other half of the specimen left in open, ambient conditions without additional moisture added. In a similar way to the samples in Table 3.2, the results indicate that the samples with additional moisture consistently experienced higher percent carbon absorption.

The samples in Table 3.4 were also prepared in pairs in a similar fashion to the samples in Table 3.3. Note the average percent carbon absorption might be 1 to 2% lower than that of samples in Tables 3.2 and 3.3, and that might have been the results of the samples might have been corrected for different backgrounds using a conservative method. Still, the percent carbon absorption was consistent and significant. In addition, the results also indicate that the samples with additional moisture showed higher percent carbon absorption than the ones did not receive extra moisture, which is consistent with the results from Tables 3.2 and 3.3.

By comparing the percent carbon absorption in open samples and in covered samples, it was found that the percent carbon absorption in the covered samples was slightly higher than that in the open samples, which might have been the results of assumptions made previously. When estimating the percent carbon absorption in the samples, the assumption was made that there is no carbonation inside the samples in the forms of solid calcite. This might be appropriate for covered samples because there was not enough carbon dioxide present to from $CaCO_3$ due to the covers. However, for the open samples, the assumption may not be proper. They may have already experienced carbonation to some extent since the samples have access to CO_2 in the air which is enough for the carbonation to take place. If some carbonation has occurred, then the actual percent carbon absorption of species other than calcite would be much higher in the open samples.

Every sample in Table 3.5 was prepared identically into two parts of powder form with no extra water drops during the preparation and was heated to 700° C. The percent carbon absorption in the covered samples was much higher than that in the open samples. At this temperature, the calcium carbonate might have been dissociated if there is carbonation going on in the cement samples and the assumptions to estimate the percent carbon absorption might not be appropriate. Also, the CO₂ correction factor might not be accurate enough to correlate the CO₂ amperages to CO₂ moles. This would request more future work to modify the percent carbon absorption.

In summary, all the different types of cement samples had similar results. At least 3 to 10% of the stoichiometric carbon dioxide absorption was taking place in other forms than solid calcium carbonate in all the samples. This indicates that the CO_2 is absorbed into the concrete and readily reaches an equilibrium condition with various absorbed species. Regardless of the aging condition, there is a small but significant amount of calcite stoichiometric potential for the absorbed CO_2 . This amount of carbon dioxide might be small in a single piece of concrete. On a global basis, however, it is a huge amount of carbon absorption. If 3 to 10% of the stoichiometric carbon dioxide is absorbed in other forms than solid calcium carbonate in the cement, then 2 to 6% of the cement mass, at a minimum, is comprised of other forms of CO_2 . Based on the global cement manufacturing capacity from USGS in 2005, there were at least 50

to 150 million tons of CO_2 absorbed in the cement paste in other forms in addition to solid calcium carbonate yearly.

Furthermore, if the equilibrium of absorbed CO_2 can be modified and enhanced, then it might provide a better insight to improve the sustainability of concrete and global climate change.

CHAPTER 4 <u>EARLY AGE CALCIUM HYDROXIDE FORMATION IN NOVEL</u> <u>SUSTAINABLE CONCRETE USES</u>

It was previously mentioned that water desorption curves showed two significant spikes over the duration of TPD analysis. One spike of the water desorption curve was under 200°C, which was expected to be the release of free and absorbed water in the hydrated cement paste based on previous studies. A second water spike after 400°C is the indicator of the dissociation of calcium hydroxide, which was not found in all the hydrated cement samples.

This chapter focuses on the circumstances under which the formation of calcium hydroxide would take place and the mass balances around the second water spike of water desorption curve during various TPD experiments. This might help to explain that the impact that environmental conditions might have on the early age formation of calcium hydroxide in novel cement and concrete mixes as compared to traditional concrete uses in contact with the ambient environment.

This chapter covers the following sections:

- Section 4.1, Water Amperages from TPD, will depict the water desorption curves for open samples which did not show the presence of Ca(OH)₂ and covered samples which otherwise showed the presence of Ca(OH)₂, respectively.
- Data Acquisition, Section 4.2, will demonstrate how to convert the amperages of water recorded during the TPD analysis to corresponding masses at lower temperature ranges.
 Also, the water losses need to be categorized into different regions to account for different types of desorption.
- Section 4.3, Results, will show how to interpret the data based on the calculations from Section 4.2 and how to relate to the amount of Ca(OH)₂ formation in the cement paste.

- Discussions, **Section 4.4**, will discuss the interpreted results, the conditions under which Ca(OH)₂ would be forming, and the impacts on the chemistry of hydrated cement paste.

4.1 Water Amperages from TPD

After synchronizing the amperage data files from the mass spectrometer to the temperature data files from the thermocouple based on the same time series, the amperages were normalized to a constant total pressure of 1x10⁻⁶ torr in the bleed stream. Typical depictions of the temperature ranges of water desorption during the TPD experiments for the normalized amperages recorded for masses 18 are shown in Figures 4.1 and 4.2. These samples were all heated to 700°C. Figure 4.1 depicts a representative set of the open samples, both ambient and oven, while Figure 4.2 depicts a complementary set of the covered samples, both ambient and oven.



Figure 4.1: Water desorption curves for typical ambient open (AO) and oven open (OO) samples.



Figure 4.2: Water desorption curves for typical ambient covered (AC) and oven covered (OC) samples.

Pairs of open samples and comparable covered samples were analyzed for water desorption in this experiment. Water was constantly being desorbed from the samples, but there were two temperature ranges (25°C-350°C and 350°C-500°C) which showed significant desorption. For both ambient and oven covered samples (Figure 4.2), there were water spikes in both ranges, whereas for both ambient and oven open samples (Figure 4.1), there was only one spike in the earlier range. Past experiments indicated that the earlier spike was due to the water desorption from the free absorbed water, interlayer water or from C-S-H gel, the latter spike was due to the calcium hydroxide dissociation and subsequent desorption (Equation 4.1).

$$Ca(OH)_{2(s)} \to CaO_{(s)} + H_2O_{(g)} \tag{4.1}$$

4.2 Data Acquisition

The data acquisition process for H_2O was similar to what was discussed in Section 3.2. All the amperages resulted from TPD analysis were first normalized based on a constant total pressure of 1×10^{-6} torr in the bleed stream. These normalized amperages were added over the duration of each analysis to give an integrated total of amperages for each of the two molecular weight ranges: 17.5-18.5 for H_2O and 39.5-40.5 for Ar. The molar percents of water in the bleed stream with respect to argon were determined by the ratios of the summed amperages for water to argon using an appropriate correction factor for H_2O . Then the total moles for H_2O were determined by multiplying by the constant argon flow rate through the reactor over the duration, and calculating the masses based on the molecular weights.

As previously mentioned, the water desorption curve might have two spikes over the duration of the TPD analysis, with one spike under 200° C which based on previous studies is expected to be the release of free and absorbed water in the hydrated cement paste and a second water spike after 400° C which is indicative of the dissociation of calcium. To analyze the extent of water desorption in these two different temperature ranges, H₂O mass losses from these two different temperature ranges need to be calculated and compared.

In order to easily compare the results, water mass losses due to desorption were divided into several categories. Figure 4.3 depicts a typical water desorption curve from the covered hydrated cement sample, ACXX6Pb, which was in coarse powder form for the TPD analysis.



Figure 4.3: Typical water desorption curve depicting areas of different temperature ranges and desorption phenomena of interest (Sample ACXX6Pb).

 $L1_{H2O}$, $L2_{H2O}$, and $L3_{H2O}$ represent the total water mass losses from TPD test at temperature range of 25°C-350°C, 350°C-500°C, and above 500°C, respectively, while LT_{H2O} represents the total water losses over the entire TPD test. These water losses were calculated

using Equation 3.3
$$\sum_{\Delta t} \left[\left(\frac{molesH_2O}{molesAr} \right) \cdot \left(\frac{50ccAr}{min} \right) \cdot \left(\frac{1molAr}{22400ccAr} \right) \cdot \left(\frac{18gH_2O}{molesH_2O} \right) \right] = L_{H_2O} \text{ for each } C_{H_2O}$$

respective range. The total water losses over the duration of the experiments would be:

$$LT_{H,O} = L1_{H,O} + L2_{H,O} + L3_{H,O}$$
(4.2)

However, in the second temperature range, there can be water desorption from calcium hydroxide dissociation as well as other phenomena. In order to calculate the proportion of this water loss from the calcium hydroxide dissociation, the second water loss range represented by $L2_{H2O}$ is further divided into subsections *a* and *b* as in Figure 4.3. A constant slope line has been used to separate the two regions based on the water desorption curves for both covered samples (Figure 4.2) and for open samples (Figure 4.1). It was noted that the water desorption other than that contributed from calcium hydroxide was decreasing in a nearly constant rate after the first water spike. $L2a_{H2O}$ is estimated as the water from calcium hydroxide dissociation, and it is equal to zero for most open samples. $L2b_{H2O}$ was calculated by using the average mass loss under the linear portion as in Figure 4.3 and $L2a_{H2O}$ was calculated by subtracting $L2b_{H2O}$ from $L2_{H2O}$. All the water masses were divided by corresponding post-TPD masses to make them more comparable based on the total unit mass of cement in each of the samples ($L_{H2O}/M_{TPD-post}$).

4.3 Results

Based on the two different types of water desorption curves for the hydrated cement paste samples when heating up to 700° C, this section will show the statistical data on the water desorption spikes for all the samples in this experiment (Section 4.3.1), list the results for the paired sample sets as groups (Section 4.3.2), and quantify the calcium hydroxide in the samples (Section 4.3.3).

4.3.1 Statistical Data on Water Desorption Spikes

Most of the open samples, for both ambient and oven, did not have a second water spike while most of the covered samples did have two spikes. This very interesting result implies that calcium hydroxide may not be forming in the open samples. Therefore, in addition to the 16 pairs of water desorption samples used for this experiment, a set of 50 additional open samples also was included in a statistical analysis with regard to the existence of the second H_2O desorption spike and whether they were aged open or covered. The results are in Tables 4.1 and 4.2. Less than 10% of the open samples showed any spike in the second temperature range, while almost 90% of the covered samples had this spike.

TPD Dates	Age (months)	with Fly Ash or Not	Number of Samples	Number of Samples WITH a Second H ₂ O Spike		
Eab 2008	1.0	NO	4	0		
red, 2008	2.8	NO	4	0		
Mor. 2008	1.8	NO	8	0		
Wiai, 2008	3.7	NO	8	0		
Apr(1), 2008	5.0	NO	12	6		
Amr(2) = 2008	3.7	NO	8	0		
Apt(2), 2008	3.7	YES	8	0		
June, 2008	5.7	NO	7	0		
July, 2008	6.8	NO	7	0		
Total			66	6		
Percent of Total				9.09%		

 Table 4.1: Presence of Second Water Desorption Spike in Open Samples.

Table 4.2: Presence of Second Water Desorption Spike in Covered Samples.

TPD Dates	Age (months)	with Fly Ash or Not	Number of Samples	Number of Samples WITHOUT a Second H ₂ O Spike
Eab 2008	1.0	NO	4	1
reb, 2008	2.8	NO	4	1
June, 2008	5.7	NO	8	0
Total			16	2
Percent of Total				12.5%

4.3.2 Water Desorption Hydrolysis Results

To analyze the extent of water desorption in the two different temperature ranges, $25-350^{\circ}$ C and $350-500^{\circ}$ C, H₂O mass losses from those two temperature ranges need to be calculated and compared. Paired sets of the covered and open samples were also compared for determination

of the extent of hydrolysis, i.e., similar sets of covered samples which showed a second water spike were paired with sets of open samples which were aged under otherwise comparable conditions and for the same time period as the corresponding covered samples. For example, in the first pairing, a set of the two 1.0-month old ambient covered samples were each split in two and then paired with two split ambient open samples having otherwise the same aging conditions and all prepared similarly for TPD analysis (except as noted with the 'C' or 'W' if in chunk or coarse powder form) and heated to 550°C. The second pairing were ambient covered and open samples aged to 2.8 months and heated to 700°C, and the fourth pairing were oven covered and open samples aged to 5.7 months and heat to 700°C. The split samples in the first two pairings received the chunk versus powder treatment, while the third and fourth pairings were all prepared in coarse powder form. These paired sample sample samples age age up samples age age to 3.8.

4.3.3 Calcium Hydroxide Formation

Even though the ratio of the water mass losses to the post-TPD masses in the samples give some indication of the range of calcium hydroxide formation in each sample, it cannot be directly used in comparing the samples. This is because there are multiple reactions occurring within the samples during aging, with both water and carbon dioxide absorbing, desorbing and/or reacting with the cement paste and therefore the actual moles of calcium within each sample cannot be determined without some simplifications and assumptions. The purpose of this section is to estimate the proportion of calcium hydroxide formation in the covered hydrated cement paste by analyzing with respect to the mole fraction as compared to the available calcium ions in the cement paste.

et	lahal#	Age	Test Final			L _{H20} /M _T	PD-post			
Š	Label #	(month)	Temp (°C)	L1 _{H20}	L2a _{H20}	L2b _{H20}	L2 _{H20}	L3 _{H20}	LT _{H20}	L2 _{H20} /L1 _{H20}
	ACXX7PC	1.0	550	0.064	*_	-	0.010	0.002	0.077	0.163
	ACXX7PW	1.0	550	0.070	0.003	0.007	0.011	0.003	0.083	0.154
	ACXX9PC	1.0	550	0.093	-	-	0.008	0.004	0.104	0.084
ir1	ACXX9PW	1.0	550	0.091	0.000	0.006	0.006	0.001	0.099	0.068
Ра	AOX31PC	1.0	550	0.034	**NP	0.002	0.002	0.001	0.037	0.045
	AOX31PW	1.0	550	0.037	NP	0.002	0.002	0.001	0.040	0.054
	AOX36PC	1.0	550	0.038	NP	0.001	0.001	0.000	0.040	0.029
	AOX36PW	1.0	550	0.040	NP	0.002	0.002	0.001	0.043	0.059
	AC7C	2.8	550	0.051	-	-	0.011	0.002	0.065	0.217
	AC7W	2.8	550	0.048	0.005	0.004	0.009	0.001	0.059	0.189
2	AC8W	2.8	550	0.052	0.000	0.004	0.004	0.002	0.058	0.077
air	AO8C	2.8	550	0.052	NP	0.003	0.003	0.002	0.056	0.061
Δ.	AO8W	2.8	550	0.049	NP	0.003	0.003	0.001	0.053	0.065
	AO9C	2.8	550	0.066	NP	0.003	0.003	0.001	0.070	0.045
	AO9W	2.8	550	0.067	NP	0.003	0.003	0.002	0.072	0.048
	ACXX6Pa	5.7	700	0.078	0.005	0.011	0.016	0.002	0.096	0.209
	ACXX6Pb	5.7	700	0.093	0.006	0.014	0.020	0.007	0.120	0.215
	ACXX8Pa	5.7	700	0.050	0.002	0.006	0.008	0.001	0.060	0.162
ir3	ACXX8Pb	5.7	700	0.056	0.002	0.006	0.008	0.001	0.065	0.142
Ра	AOX37Pa	5.7	700	0.054	NP	0.005	0.005	0.002	0.061	0.091
	AOX37Pb	5.7	700	0.056	NP	0.006	0.006	0.000	0.063	0.105
	AOX38Pa	5.7	700	0.048	NP	0.004	0.004	0.000	0.052	0.079
	AOX38Pb	5.7	700	0.059	NP	0.005	0.005	0.002	0.065	0.083
	OCXX6Pa	5.7	700	0.063	0.011	0.013	0.023	0.005	0.091	0.375
	OCXX6Pb	5.7	700	0.053	0.010	0.012	0.022	0.006	0.081	0.422
4	OCXX8Pa	5.7	700	0.056	0.012	0.010	0.022	0.004	0.082	0.393
air	OCXX8Pb	5.7	700	0.046	0.011	0.010	0.021	0.004	0.072	0.455
L T	OOX36Pa	5.7	700	0.037	NP	0.003	0.003	0.001	0.041	0.092
	OOX36Pb	5.7	700	0.032	NP	0.003	0.003	0.001	0.037	0.100
	OOX38Pa	5.7	700	0.031	NP	0.003	0.003	0.001	0.035	0.110

 Table 4.3: Water Desorption Masses for Paired Samples at Different Ages.

* - means not analyzed for samples in chunk form;
** NP means no second peak was found in the corresponding sample.

Before determining how much calcium hydroxide is formed in the cement samples, there are some assumptions which need to be made:

- (1) Carbonation, the formation of calcium carbonate (CaCO₃), for most concrete uses mimicked by the covered samples is relatively small due to the inaccessibility of carbon dioxide and is a diffusion limited process. So carbonation is assumed negligible.
- (2) In actuality, many cement samples may have around 10% of CO₂ absorbed in other forms other than calcium carbonate, but it can be assumed that most of this CO₂ was desorbed by 550°C and 700°C. Therefore, the post-TPD masses for these covered samples do not have either significant CO₂ or H₂O, which means the post-TPD masses are similar to the initial cement sample composition, with 61% of CaO by mass.

Based on these assumptions, sets of the covered samples can be analyzed for the same final test temperature by applying the following equations:

Equation 4.3 is used to determine the mass fraction of H_2O in the form of $Ca(OH)_2$ to CaO:

$$w_{H_2O-CH/CaO} = \frac{m_{H_2O-CH}}{m_{CaO}} = \frac{m_{H_2O-CH}}{m_{TPD-post} \times 61\%} = \frac{L2a_{H_2O}}{m_{TPD-post} \times 61\%}$$
(4.3)

Where:

- $w_{H_2O-CH/CaO}$ is the mass fraction of water in the form of calcium hydroxide as a mass ratio to calcium oxide,
- $m_{H,O-CH}$ is the mass of water in the form of calcium hydroxide,
- m_{CaO} is the mass of calcium oxide, and
- $m_{TPD-post}$ is the post TPD mass of the sample as previously noted.

Equation 4.4 is used to determine the mole ratio of H_2O in Ca(OH)₂ to CaO in a sample:
$$x_{CH/CaO} = \frac{n_{H_2O-CH}}{n_{CaO}} = \frac{m_{H_2O-CH}/18}{m_{CaO}/56} = w_{H_2O-CH} \frac{18}{56} = 0.32w_{H_2O-CH}$$
(4.4)

Where:

- $x_{CH/CaO}$ is the mole fraction of calcium hydroxide to available calcium oxide,
- n_{H_2O-CH} is the moles of water in the form of calcium hydroxide, and
- n_{CaO} is the moles of calcium oxide or calcium.

Using the above equations, and averaging for each set of covered samples in Table 4.3, the average mole fraction of calcium hydroxide formation in early age cement can be derived for the various aging ages. These are listed in Table 4.4:

Table 4.4: Average Mole Ratios of Ca(OH)₂ to CaO in Covered Cement Samples.

Label #	Age (month)	Test Final Temp (°C)	X _{CH/CaO}
AC1.0	1.0	550	0.009
AC2.8	2.8	550	0.012
AC5.7	5.7	700	0.021
OC5.7	5.7	700	0.056

Note: AC1.0 represents the average of the 1.0-month old ambient covered samples, AC2.8 the 2.8-month average, etc.

Then the relationship between this mole fraction and aging time is plotted in Figure 4.4

with a linear approximation given for the ambient sets.



Figure 4.4: Mole fraction of calcium hydroxide to calcium oxide in covered cement samples.

4.4 Discussions

This section covers the discussion on the frequency of $Ca(OH)_2$ formation from the statistical data (Section 4.4.1), and quantitive analysis of absorbed water and $Ca(OH)_2$ formation in the samples (Sections 4.4.2 and 4.4.3), respectively.

4.4.1 Statistical Analysis on Ca(OH)₂ Frequency

For all the open samples, more than 90% of them do not have a second water spike (Table 4.1). One plausible reason for this is that most of these samples are open to the air immediately after preparation and have fairly rapid, and significant water evaporation, which limited the availability of water and therefore the potential for formation of $Ca(OH)_2$. Moreover, the open samples have more surface area, which makes the CO_2 more accessible and accelerates the carbonation process (Equation 4.5) in the hydrated cement paste.

$$Ca^{2+} + CO_3^{2-} \to CaCO_3 \tag{4.5}$$

However, there were six 5.0-month old samples (less than 10%) that had second water spikes. They were all 2.9-month old oven open samples. These were also furthered analyzed as to the percent of calcium hydroxide formation with respect to the available calcium oxide using Equation 4.4. The results are in Table 4.5 with an average mole ratio of 0.006. This value is much less than the ambient covered sample of comparable age and significantly less than a comparable covered oven sample would be at this age based on interpolation of the values in Figure 4.4. Note that in the values in Table 4.5, the assumption is still made that carbonation is negligible in the post TPD mass, which might not be accurate. However, the values still give some indication of the relative water quantities.

Label # Age (month	A = -	Age (months) Test Final Temp (°C)	$L_{H2O}/M_{TPD-post}$						
	Age (months)		L1 _{H20}	$L2a_{H2O}$	$L2b_{H2O}$	L3 _{H20}	LT _{H20}	L2 _{H2O} /L1 _{H2O}	X _{CH/CaO}
OO16WD	2.9	450	0.0582	0.0004	0.0036	0.0019	0.0641	0.069	0.002
OO16WN	2.9		0.0275	0.0015	0.0038	0.0014	0.0342	0.192	0.008
OO17WD	2.9	500	0.0853	0.0001	0.0049	0.0022	0.0925	0.059	0.000
OO17WN	2.9		0.0329	0.0022	0.0029	0.0010	0.0390	0.155	0.011
OO28WD	2.9	550	0.0839	0.0001	0.0049	0.0068	0.0957	0.060	0.001
OO28WN	2.9		0.0349	0.0027	0.0036	0.0021	0.0433	0.182	0.014

Table 4.5: Analysis of Open Samples with Second Water Spikes.

4.4.2 Water Desorption Hydrolysis Analysis

Table 4.3 lists H₂O desorption of typical paired-up different aged samples from TPD at different temperature ranges, which basically focuses on the ambient samples. The table gives $L1_{H2O}$, $L2_{H2O}$, and $L3_{H2O}$ for all the samples listed in the table. It also provides values of $L2a_{H2O}$ and $L2b_{H2O}$ for the covered samples in powder form.

Note that the lower temperature desorption ratio $(L1_{H2O}/M_{TPD-post})$ is fairly constant for similar samples, however, there are some variations since some of the samples received drops while others did not and the addition of water prior to testing would allow for some variation in

this region of absorbed water. In contrast, the mid-range temperature desorption ratio $(L2_{H2O}/M_{TPD-post})$ varies significantly among different types of samples. Basically, $L2_{H2O}$ is much larger for the covered samples than for the open samples, indicating that there is very limited formation of calcium hydroxide under the conditions similar to those which would be experienced by certain novel concrete uses such as pervious concrete. The highest temperature desorption ratio $(L3_{H2O}/M_{TPD-post})$ is always very small indicating that above 500°C, most forms of water have already been desorbed from concrete. In general, $L1_{H2O}/M_{TPD-post}$ accounts for the major portion of the total water loss, about 80% of the total for the ambient covered (AC) samples, and 90% of the total for the ambient open (AO) samples.

4.4.3 Calcium Hydroxide Formation Analysis

Plotting the mole fraction of calcium hydroxide to calcium oxide in the covered samples against aging time results in a significant positive relation (Figure 4.4) (the correlation coefficient was 0.99). Ordinary least-squares simple linear regression gives a best-fit line of $x_{CH/CaO} = 0.25t + 0.58$, indicating a sensitivity of 25% mole fraction $x_{CH/CaO}$ of calcium hydroxide to available calcium oxide per month (*t*).

Comparing the ambient covered samples and the oven covered samples at 5.7 months, the mole ratio for the oven covered samples is almost triple that for the ambient covered samples. This might be due to the favorable reaction kinetics in the oven environment, where both higher relative humidity and higher temperature would enhance the water diffusion rate into the cement paste system, as well as the reaction rate to form calcium hydroxide. This analysis assumed negligible carbonation (formation of calcium carbonate) of the samples and there would need to be corrections to the analysis if this is found not to be the case. The results of the TPD experiments indicate that only the covered cement samples have significant occurrences of the water spike from $Ca(OH)_2$ dissociation, while most of the open cement samples do not. This can be explained by several phenomena including the higher availability of water in the covered samples (less evaporation) than in the open samples, and also by the competition for reaction with carbon dioxide in the open samples limiting the available sites for calcium hydroxide formation and changing (lowering) the pH, an important variable in the carbonate system equilibrium equations.

The results also confirm the common assumption that the water spike at about 150° C is due to the loss of water that absorbed in the cement paste, and the water spike at about 450° C is due to the loss of water that from Ca(OH)₂ decomposition. However, since the second spike is not occurring frequently in the open samples, interpretation of results from TPD experiments in the middle temperature ranges will need to be modified for experiments on these novel concrete uses with more surface area exposure such as pervious concrete.

Ordinary least-squares simple linear regression for mole ratio of $Ca(OH)_2$ to the available CaO in the cement paste demonstrated that the mole ratio was increasing as the aging time goes on and gives some indication of the rate of this reaction. The mole ratio of $Ca(OH)_2$ to the available CaO for the oven covered samples was greater than that for the ambient covered samples, which indicates that temperature and relative humidity have influence on the reaction rate to form $Ca(OH)_2$.

In summary, the results from this portion demonstrate that there is $Ca(OH)_2$ existence in traditional concrete uses while not in novel concrete uses. This might help us to further understand the concrete chemistry in novel concrete uses, explain the principle for carbonation

process, and search a way or environmental condition to accelerate/discourage carbonation in novel concrete uses.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

The Temperature Programmed Desorption (TPD) system was used in this research to investigate the carbon dioxide and water speciation in the hydrated cement paste samples. The results form the following conclusions:

(1) Carbon Dioxide Absorption Potential in Concrete

The CO_2 results of the TPD analysis and estimated percent carbon absorption in concrete indicate the following:

- Fairly young cement pastes, when ground and exposed to air, have a significant amount of carbon species (3-10%) absorbed other than in the form of calcite;
- Samples which have been aged in the ambient environment have slightly higher percent carbon absorption than those that have been aged in the oven environment;
- Samples which have some additional moisture added and are exposed to air have slightly increased amounts of these absorbed carbon species;
- The estimated percent carbon absorption in covered samples is slightly higher than that in open samples based on the assumptions and the way to estimate it.

This research does show that alternative absorbed carbon dioxide species do exist in cement paste samples in amounts that are significant with respect to the stoichiometric potential for reversing the calcination process.

(2) Early Age Calcium Hydroxide Formation in Novel Sustainable Concrete Uses

The water desorption hydrolysis analysis concludes the following:

- This research does confirm that most of the water in cement pastes which will be released around 150°C is the free absorbed water, and the decomposition of Ca(OH)₂ occurs around 450°C;

- The solid calcium hydroxide dissociation spike in the TPD analysis which was expected to occur around 450°C did not occur for most of the open samples, which indicates that the potential for the formation of calcium hydroxide solid phase was limited due to the preference for carbonation under those conditions;
- In addition, water was still in the specimens, and calcium oxide hydration is usually expected to occur under these circumstances. There is an indication that calcium hydroxide and calcium carbonate exist in cement pastes not just as their solid phases, but also as 'hydrated' complexes or absorbed species of these compounds;
- The mole ratio of calcium hydroxide to the available calcium oxide (higher for oven samples) implies that temperature and relative humidity might influence the reaction rate to form calcium hydroxide.

(3) Broader Impacts

According to the most recent survey of Portland Cement Association (PCA) members, an average of 927 kg (2044 lb) of CO₂ is emitted for every 1000 kg (2205 lb) of Portland cement produced in the US (Marceau et al. 2006). If there is 3 - 10% of CO₂ absorbed in the cement paste in other forms, then an average of 60 -200 kg (130 – 440 lb) of CO₂ is absorbed by every 1000 kg (2205 lb) of Portland cement produced. This means, globally, there would be at least 150 - 500 million tons of CO₂ absorbed in the cement in addition to carbonation every year. In other words, there would be a significant amount of CO₂ sequestration by Portland cement, which will have a significant impact on the global climate change.

(4) Recommendations for Future Work

There are some potential problems associated with this experimental setup. For example, the average percent difference between the weighed mass changes and calculated mass losses for

samples heated to 700°C is -10%. The following are some recommendations for future related work:

- Prepare the sample in powder form in the environment without CO₂, for example, nitrogen environment;
- Use glass containers and lids other than the plastic cuvettes because the cuvettes might have organic carbon in its ingredient which could leach organic carbon into the samples over time and contaminate the samples;
- Minimize the exposure time since more CO₂ could be absorbed in the samples and H₂O in the samples could evaporate rapidly due to the large surface area in powder form;
- Calibrate the correction factors for H₂O and CO₂ correctly and appropriately due to the significance of them in calculating the mass losses;
- Apply certain equipment factor for TPD to correct the system errors since the analyzer may not be accurate or sensitive after passing 550°C.

NOTATION

- $\circ \quad CF_{H2O}-Correction \ factor \ for \ H_2O$
- \circ CF_{CO2} Correction factor for CO₂
- o L_{H2O} Total water mass losses from TPD test over delta time or delta temperature
- o L_{CO2} Total CO₂ mass losses from TPD test over delta time or delta temperature
- LT Total calculated mass losses from TPD test
- \circ LT_{H2O} Total water mass losses from TPD test
- \circ L1_{H2O} Total water mass losses from TPD test at 25°C-350°C temperature range
- \circ L2_{H2O} Total water mass losses from TPD test at 350°C-500°C temperature range
- \circ L2a_{H2O} Total water mass losses from TPD test at 350°C-500°C temperature range assumed to be from Ca(OH)₂ dehydration
- \circ L2b_{H2O} Total water mass losses from TPD test at 350°C-500°C temperature range assumed not to be from Ca(OH)₂ dehydration
- $\circ~~L3_{H2O}$ Total water mass losses from TPD test at temperature range above 500°C
- \circ m_{hc} Mass of hydrated cement samples
- \circ m_{TPD-pre} Analysis sample masses before TPD test
- \circ m_{TPD-post} Analysis sample masses after TPD test
- \circ m_{H2O-CH} Water desorption mass from calcium hydroxide
- \circ m_{CaO} Calcium oxide mass
- \circ n_{H2O-CH} Water desorption moles from calcium hydroxide
- \circ n_{CO2} Moles of CO₂ released after the TPD analysis
- \circ n_{CaO} Moles of calcium oxide

- $x_{CH/CaO}$ Mole fraction of calcium hydroxide to available calcium oxide in cement paste
- $w_{H_2O-CH/CaO}$ Mass fraction of water in the form of calcium hydroxide to available calcium oxide in cement paste
- %Carb Percent carbon absorption
- %Difference Percent difference of mass losses between the weighed masses and calculated masses
- \circ $\Delta Mass_{weigh}$ Difference between pre-TPD mass and post-TPD mass

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APPENDICES

APPENDIX 1 CALIBRATION FOR CONSISTENCY

The calibration process was required every time running the TPD analysis to make sure it was consistent on the TPD system. The purpose to check this consistency was to make sure that the total pressure leakage was in linear relationship with the amperages of calibrated compounds. This section focuses on the calibration of CO_2 gas.

The gas content used in the calibration process was 30% CO₂ gas. By adjusting the leakage rate several times, the various CO₂ amperages at different leakage pressures can be generated. Then when plotting the averaged CO₂ amperages versus the averaged pressure in torr, the data should fit in a linear relationship. The slope would give the response factor (RF) for the mass spectrometer. Figure A1.1 gives the typical depiction of this method based on the calibration result on June 30^{th} , 2008.



Figure A1.1: RF calibration on TPD system on June 30th, 2008.

If the system was consistent along with consecutive experiment trials, then the RF should be consistent or the same for each calibration result. Table A1.1 lists the RF results for the trials on June as well as the R^2 value.

Date	RF	\mathbf{R}^2	
04/05/08	1.232	0.996	
04/06/08	1.232	0.999	
04/07/08	1.292	0.999	
04/08/09	1.152	0.998	
04/24/08	1.204	0.998	
04/25/08	1.216	0.997	
06/25/08	1.155	0.995	
06/30/08	1.318	0.999	
07/01/08	1.249	0.999	
07/02/08	1.311	1.000	
07/29/08	1.162	0.998	

Table A1.1: Calibration for Consistency Based on RF Results.

It was noted that the RF values, which were around 1.22, were consistent during the experiment period. That means the mass spectrometer and analyzer were consistent on detecting the CO_2 content in the gas bleed stream.

APPENDIX 2 CALIBRATION FOR DATA ANALYSIS

It was noticed that the percent difference of mass losses between the weighed mass changes and calculated masses was out of the range of -10%~10% when analyzing the data from TPD results. The reasons for this problem might be: (1) the weighed masses might not be precise due to the precision of the scale; (2) the assumption $\frac{\text{molesH}_2\text{O}}{\text{molesAr}} = \frac{\text{ampsH}_2\text{O}}{\text{ampsAr}}$ may not be accurate since many of the species may be modified or split by the analyzer and then sensed at different molecular weights. Therefore, there was necessity to find a calibration method to make the results as precise as possible.

In the calibration process for this research, two methods were used: correction factor method and response factor (RF) method. Only H_2O results were calibrated in this calibration process since CO_2 was concentrated around molecular weight of 44 and it was difficult to calibrate CO_2 results separately. However, the correction factor for CO_2 was considered during the analyzing procedure.

A2.1 Correction Factor Method

Several random paired up samples (including ambient, oven, open, and covered samples) were selected to run the TPD analysis, and the samples were heated only to 350°C with an ramp rate of 10°C/min. Up till this temperature, only H₂O and small amounts of free absorbed CO₂ can be released from the samples based on previous studies, and the CO₂ mass losses can be ignored. In this case, the weighed mass changes $\Delta mass_{weigh}$ should be equal to the calculated water mass losses $L_{H,O}$. If not, a constant equipment correction factor of H₂O (CF_{H,O}) will be needed to

calibrate and get $\Delta mass_{weigh}$ and L_{H_2O} close enough. Using this correction factor, the Equation A2.1 can be obtained:

$$\frac{\text{molesH}_2\text{O}}{\text{molesAr}} = CF_{\text{H}_2\text{O}} \frac{\text{ampsH}_2\text{O}}{\text{ampsAr}}$$
(A2.1)

(A2.2)

Therefore, $\Delta mass_{weigh}$ = $CF_{\rm H_2O}L_{\rm H_2O}$ using Equation A2.2

$$(CF_{H_2O} \frac{ampsH_2O}{ampsAr}) \cdot (\frac{50ccAr}{min}) \cdot (\# \min) \cdot (\frac{1molAr}{22400ccAr}) \cdot (\frac{18gH_2O}{molesH_2O}) = L_{H_2O} = \Delta mass_{weigh}$$

Then for CO₂ analysis, an equipment correction factor of CO₂ CF_{CO_2} can be introduced

to correct the CO_2 amperages (as in Equation A2.3).

$$\Delta mass_{weigh} = CF_{H_2O}LH_2O + CF_{CO_2}LCO_2$$
(A2.3)

Table A2.1 lists the samples used for this calibration process. The column of $(L_{CO2}/L_{H2O})*100$ shows the ratio of CO₂ mass losses to H₂O mass losses at this temperature range; the K_{H2O} column shows the correction factor for the H₂O based on Equations A2.1 and A2.2; the ratio column shows the ratio of weighed mass loss changes to the calculated mass losses using the correction factor.

Sample	$(L_{CO2}/L_{H2O})*100$	CF _{H2O}	*Ratio
Number	(%)		(%)
ACXX1PW	8.949	1.456	106.526
OCXX1PW	11.674	1.563	99.689
ACXX2PW	7.136	1.535	101.413
OCXX2PW	10.651	1.555	100.168
AOX16PW	4.667	1.560	99.841
OOX16PW	7.843	1.589	98.122
AOX17PW	5.357	1.657	94.145
OOX17PW	7.047	1.544	100.799
Average	7.915	1.557	100.088

Table A2.1: Results of Samples Used for Calibration Process.

* Ratio= $\Delta mass_{TPD} / \Delta mass_{weigh}$ *100

From the table, the average value of CF_{H2O} is 1.557.

For this calibration, although there was not much CO_2 coming out of the cement samples which were selected to do water calibration analysis (average L_{CO2}/L_{H2O} ratio is 7.915%), the CO_2 results were still considered when calculating K_{H2O} . The *LT* to $\Delta mass_{weigh}$ ratio turned out to be close to 100% (the average ratio was 100.088%).

From one published paper (INFICON 2008), the material factor (MF) of H_2O is 1.33, and MF of CO_2 is 1.02. To make sure these factors worked well for the TPD results in this experiment, some iteration needed to be done for the last three sets of experiments which were finished in April and June. Table A2.2 lists the specific iteration:

By comparing the correction factors in Table A2.2, it was noted that the published value of material factor for H₂O and CO₂ kept the average %lower ratio within the range of $\pm 10\%$, which was the best for the later calibration in this experiment.

CF _{H2O}	CE	Average % lower Ratio					
	CF _{CO2}	1-Apr	2-Apr	June			
1.636	0.900	-30.222	-5.709	-7.838			
1.636	1.020	-31.273	-8.563	-16.280			
1.636	1.124	-32.184	-11.035	-23.596			
1.557	0.900	-24.314	-1.638	-3.320			
1.557	1.020	-25.365	-4.491	-10.938			
1.557	1.124	-26.276	-6.964	-17.539			
1.33	0.900	-7.340	10.060	0.490			
1.33	1.020	-8.391	7.207	-7.952			
1.33	1.124	-9.302	4.734	-15.269			
1.0	1	16.461	24.689	2.435			
1.1	1	8.984	19.535	-0.286			
1.2	1	1.506	14.382 -0.606				
1.1	1.124	7.897	16.587	-9.009			
1.2	1.124	0.419	11.434	-11.731			
1.3	1.124	-7.058	6.280	-14.452			
1.2	0.900	2.382	16.760	5.742			
1.2	1.020	1.331	13.906	-1.876			
1.2	1.124	0.419	11.434	-8.477			
1.3	0.900	-5.096	11.606	1.306			
1.3	1.020	-6.147	8.753	-7.136			
1.3	1.124	-7.058	6.280	-14.452			

 Table A2.2: Iteration for the Correction Factor from Published Data.

* %lower Ratio= ($\Delta mass_{weigh}$ - *LT*)/ $\Delta mass_{weigh}$ *100

A2.2 RF (Response Factor) Method

Every time before starting the experiment, the calibration on TPD was run using 3000PPM CO_2 /He cylinder. This gas has to be diluted to make sure that CO_2 amps coming from TPD are within this calibration range. So, the flow rate of CO_2 /He is 15cc/min, and the flow rate of the

dilution gas He is 30cc/min. Then, by adjusting the leak valve five different total pressure torr for the calibration can be derived. Then the CO_2 response factor RF (amps/torr) can be calculated by plotting CO_2 amps versus CO_2 torr. The following figure is an example for this calibration based on the calibration result on July 2nd, 2008:



Figure A2.1: Response factor calibration method for TPD analysis on July 2nd, 2008.

The RF is equal to the slope, in this case, RF=1.31141.

There are some RF correction factors for H_2O from other users. The average value is 18.968 and 12.626, respectively (torr/amps). Table A2.3 lists the results by applying the RF from other users.

Sample Number	∆ Mass_{weigh}	*RF₁ - Liu	**RF ₂ - Hetrick	CO ₂ RF	* ∆Mass _{TPD1}	*Ratio1	** ∆Mass _{TPD2}	**Ratio2
OCXX6Pa	0.044			1.32674	0.03600	81.825	0.02490	56.589
OCXX6Pb	0.054				0.03534	65.445	0.02465	45.642
AOX38Pa	0.040				0.02560	64.000	0.01785	44.617
AOX38Pb	0.038			1.24913	0.02960	77.905	0.02044	53.789
ACXX8Pa	0.046	40.000			0.02966	64.472	0.02091	45.450
ACXX8Pb	0.044	18.968	12.626		0.03258	74.057	0.02258	51.319
OCXX8Pa	0.044				0.03200	72.724	0.02214	50.328
OCXX8Pb	0.048			1 01111	0.03295	68.645	0.02310	48.133
OOX36Pa	0.034			1.31141	0.02341	68.849	0.01630	47.955
OOX36Pb	0.036				0.02409	66.921	0.01688	46.878
Average						70.484		49.070
ACXX1PW	0.024		8 12.626	1.31339 26 1.23801	0.03547	147.805	0.02365	98.562
OCXX1PW	0.016				0.02101	131.297	0.01402	87.601
ACXX2PW	0.034	40.000			0.04641	136.510	0.03094	90.996
OCXX2PW	0.022				0.02908	132.160	0.01940	88.159
AOX16PW	0.020	10.900			0.02689	134.426	0.01791	89.569
OOX16PW	0.014				0.01948	139.178	0.01299	92.797
AOX17PW	0.024				0.03107	129.451	0.02070	86.266
OOX17PW	0.016				0.02360	147.509	0.01573	98.335
Average						137.292		91.536
OOX40PWD	0.030	18 968	12 626	1 16177	0.02165	72.181	0.01536	51.201
OOX40PWN	0.040	10.900	12.020	1.10177	0.02163	54.070	0.01522	38.057
Average						63.125		44.629

Table A2.3: Verification of RF for H₂O from Other Users.

*RF for water from Dongxia Liu; Ratio= $LT / \Delta mass_{weigh}$ *100;

**RF for water from Casey Hetrick; Ratio= $LT / \Delta mass_{weigh}$ *100.

As can be seen, the correction factors from the two different methods, correction factor and response factor, are not consistent and the ratio of calculated mass losses from the TPD to the weighed mass loss changes varies a lot. Therefore, for the purpose of accuracy and convenience, the correction factor method was chosen to calibrate the TPD data instead of response factor method by using the published data of 1.33 for H₂O and 1.02 for CO₂.

APPENDIX 3 WATER AND CARBON DIOXIDE DESORPTION CURVES

The figures in this section give typical depictions of water and carbon dioxide desorption from the TPD analysis for the amperages recorded over the temperature ranges for molecular weights of 18 and 44 respectively. The left axis represents the amperages as normalized for leak rate pressure for the mass range around 18, which represents water. The right axis is the summed amperages as normalized for leak rate pressure around 44, which represents CO₂. Figures A3.1-A3.51 depict desorption curves for the samples heated to 550°C during the TPD analysis, and Figures A3.52-A3.72 depict desorption curves for the samples heated to 700°C during the TPD analysis.



Figure A3.1: Water and CO₂ desorption curves for sample AC7C (exposure time: 22h).



Figure A3.2: Water and CO₂ desorption curves for sample AC7W (exposure time: 24h).



Figure A3.3: Water and CO₂ desorption curves for sample AO8C (exposure time: 45h).



Figure A3.4: Water and CO₂ desorption curves for sample AO8W (exposure time: 47h).



Figure A3.5: Water and CO₂ desorption curves for sample ACXX7PC (exposure time: 49h).



Figure A3.6: Water and CO₂ desorption curves for sample ACXX7PW (exposure time: 51h).



Figure A3.7: Water and CO₂ desorption curves for sample AOX31PC (exposure time: 67h).



Figure A3.8: Water and CO₂ desorption curves for sample AOX31PW (exposure time: 70h).



Figure A3.9: Water and CO₂ desorption curves for sample AC8W (exposure time: 73h).



Figure A3.10: Water and CO₂ desorption curves for sample AO9C (exposure time: 94h).



Figure A3.11: Water and CO₂ desorption curves for sample AO9W (exposure time: 96h).



Figure A3.12: Water and CO₂ desorption curves for sample ACXX9PC (exposure time: 115h).



Figure A3.13: Water and CO₂ desorption curves for sample ACXX9PW (exposure time: 118h).



Figure A3.14: Water and CO₂ desorption curves for sample AOX36PC (exposure time: 120h).



Figure A3.15: Water and CO₂ desorption curves for sample AOX36PW (exposure time: 121h).



Figure A3.16: Water and CO₂ desorption curves for sample OO18WD (exposure time: .5h).



Figure A3.17: Water and CO₂ desorption curves for sample OO18WN (exposure time: 2h).



Figure A3.18: Water and CO₂ desorption curves for sample OO19WD (exposure time: .5h).



Figure A3.19: Water and CO₂ desorption curves for sample OO19WN (exposure time: 2h).



Figure A3.20: Water and CO₂ desorption curves for sample OO20WD (exposure time: .5h).



Figure A3.21: Water and CO₂ desorption curves for sample OO20WN (exposure time: 2h).



Figure A3.22: Water and CO₂ desorption curves for sample OO21WD (exposure time: .5h).



Figure A3.23: Water and CO₂ desorption curves for sample OO21WN (exposure time: 2h).


Figure A3.24: Water and CO₂ desorption curves for sample OOX31PWD (exposure time: .5h).



Figure A3.25: Water and CO₂ desorption curves for sample OOX31PWN (exposure time: 2h).



Figure A3.26: Water and CO₂ desorption curves for sample OOX32PWD (exposure time: .5h).



Figure A3.27: Water and CO₂ desorption curves for sample OOX32PWN (exposure time: 2h).



Figure A3.28: Water and CO₂ desorption curves for sample OOX33PWD (exposure time: .5h).



Figure A3.29: Water and CO₂ desorption curves for sample OOX33PWN (exposure time: 2h).



Figure A3.30: Water and CO₂ desorption curves for sample OOX34PWD (exposure time: .5h).



Figure A3.31: Water and CO₂ desorption curves for sample OOX34PWN (exposure time: 2h).



Figure A3.32: Water and CO₂ desorption curves for sample OO27WD (exposure time: 14h).



Figure A3.33: Water and CO₂ desorption curves for sample OO27WN (exposure time: 16h).



Figure A3.34: Water and CO₂ desorption curves for sample OO28WD (exposure time: 18h).



Figure A3.35: Water and CO₂ desorption curves for sample OO28WN (exposure time: 20h).



Figure A3.36: Water and CO₂ desorption curves for sample AOX32PWD (exposure time: .5h).



Figure A3.37: Water and CO₂ desorption curves for sample AOX32PWN (exposure time: 2h).



Figure A3.38: Water and CO₂ desorption curves for sample AOX33PWD (exposure time: .5h).



Figure A3.39: Water and CO₂ desorption curves for sample AOX33PWN (exposure time: 2h).



Figure A3.40: Water and CO₂ desorption curves for sample AOX34PWD (exposure time: .5h).



Figure A3.41: Water and CO₂ desorption curves for sample AOX34PWN (exposure time: 2h).



Figure A3.42: Water and CO₂ desorption curves for sample AOX35PWD (exposure time: .5h).



Figure A3.43: Water and CO₂ desorption curves for sample AOX35PWN (exposure time: 2h).



Figure A3.44: Water and CO₂ desorption curves for sample AOX71FWD (exposure time: .5h).



Figure A3.45: Water and CO₂ desorption curves for sample AOX71FWN (exposure time: 2h).



Figure A3.46: Water and CO₂ desorption curves for sample AOX72FWD (exposure time: .5h).



Figure A3.47: Water and CO₂ desorption curves for sample AOX72FWN (exposure time: 2h).



Figure A3.48: Water and CO₂ desorption curves for sample AOX73FWD (exposure time: .5h).



Figure A3.49: Water and CO₂ desorption curves for sample AOX73FWN (exposure time: 2h).



Figure A3.50: Water and CO₂ desorption curves for sample AOX74FWD (exposure time: .5h).



Figure A3.51: Water and CO₂ desorption curves for sample AOX74FWN (exposure time: 2h).



Figure A3.52: Water and CO₂ desorption curves for sample ACXX6Pa (exposure time: .5h).



Figure A3.53: Water and CO₂ desorption curves for sample ACXX6Pb (exposure time: 3h).



Figure A3.54: Water and CO₂ desorption curves for sample ACXX8Pa (exposure time: .5h).



Figure A3.55: Water and CO₂ desorption curves for sample ACXX8Pb (exposure time: 3h).



Figure A3.56: Water and CO₂ desorption curves for sample AOX37Pa (exposure time: .5h).



Figure A3.57: Water and CO₂ desorption curves for sample AOX37Pb (exposure time: 3h).



Figure A3.58: Water and CO₂ desorption curves for sample AOX38Pa (exposure time: .5h).



Figure A3.59: Water and CO₂ desorption curves for sample AOX38Pb (exposure time: 3h).



Figure A3.60: Water and CO₂ desorption curves for sample OCXX6Pa (exposure time: .5h).



Figure A3.61: Water and CO₂ desorption curves for sample OCXX6Pb (exposure time: 3h).



Figure A3.62: Water and CO₂ desorption curves for sample OCXX8Pa (exposure time: .5h).



Figure A3.63: Water and CO₂ desorption curves for sample OCXX8Pb (exposure time: 3h).



Figure A3.64: Water and CO₂ desorption curves for sample OOX36Pa (exposure time: .5h).



Figure A3.65: Water and CO₂ desorption curves for sample OOX36Pb (exposure time: 3h).



Figure A3.66: Water and CO₂ desorption curves for sample OOX38Pa (exposure time: .5h).



Figure A3.67: Water and CO₂ desorption curves for sample OOX40PWD (exposure time: 3h).



Figure A3.68: Water and CO₂ desorption curves for sample OOX39PWN (exposure time: .5h).



Figure A3.69: Water and CO₂ desorption curves for sample OOX39PWD (exposure time: 3h).



Figure A3.70: Water and CO₂ desorption curves for sample AOX40PWN (exposure time: .5h).



Figure A3.71: Water and CO₂ desorption curves for sample AOX40PWD (exposure time: 3h).



Figure A3.72: Water and CO₂ desorption curves for sample AOX39PWD (exposure time: .5h).