THE USE OF CO_2-TREATED WASH WATER AS MIXING WATER IN CONCRETE

by

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ABSTRACT

Concrete is the most widely used construction material and the process of concrete production is responsible for the consumption of large amounts of water. Cleaning of concrete mixer trucks also consumes a massive quantity of water and it generates concrete wash water which has significant environmental and financial concerns. Reuse of wash water to produce fresh concrete is identified as a potential solution, but untreated wash water affects fresh concrete properties. The main objectives of this study are to treat wash water with carbon dioxide (CO_2) in order to eliminate the problems encountered with untreated wash water and to investigate the possibility of replacing potable water with CO_2-treated wash water for the production of concrete. This study was conducted in three phases; chemistry of wash water, mortar testing, and concrete testing. Several chemical and physical properties, such as pH, bound water contents, cation and anion concentrations in wash water, surface and bulk resistivity of concrete, and compressive strength of concrete and mortar, were analysed during this study. Freeze-thaw resistance of concrete produced with CO_2-treated wash water was also examined.

CO_2-treated wash water demonstrated impressive performance. Particularly, 75 and 100% CO_2-treatment successfully prevented further hydration of the cementitious component of wash water. Moreover, almost all concrete and mortar mixtures produced with CO_2-treated wash water displayed comparable or better results than the control mixtures. Results have shown that the solids in CO_2-treated wash water have cementitious properties and have contributed to strength development. Based on the results obtained from this study, it was concluded that CO_2-treated wash water can be used as mixing water in concrete.

DEDICATION

In memory of my beloved Dad!

ACKNOWLEDGEMENTS

It was a wonderful opportunity to pursue my graduate studies and gain research experience at the University of New Brunswick. This thesis would not have been possible without the help of the people who gave me their fullest support.

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List of Symbols, Nomenclature or Abbreviations

AAR	Alkali-aggregate reaction
AEA	Air-entraining admixture
SP	Superplasticiser
IC	Ion chromatography
ICP-OES	Inductively coupled plasma optical emission spectrometry
XRD	X-ray diffraction
SSD	Saturated-surface-dry
FTF	Fundamental transverse frequency
DF	Durability factor
C	CaO
S	SiO_2
A	Al_2O_3
F	Fe_2O_3
H	H_2O
$\underline{C}$	CO_3
$\underline{S}$	SO_3
C_xS	Calcium silicates (alite and/or belite)
C_3S	Tri-calcium silicate ($3CaO.SiO_2$), alite
C_2S	Di-calcium silicate ($2CaO.SiO_2$), belite
C_3A	Tri-calcium aluminate ($3CaO.Al_2O_3$)
C_4AF	Tetra-calcium aluminate ferrite ($4CaO.Al_2O_3.Fe_2O_3$)
CH	Calcium hydroxide (portlandite)
C-S-H	Calcium silicate hydrate
AFt	Ettringite
AFm	Calcium monosulfoaluminate

PC	Portland cement
SCM	Supplementary cementitious material
TSS	Total suspended solids
W/B	Water-to-binder ratio
W/C	Water-to-cement ratio
W/CM	Water-to-cementitious-materials ratio
TW	Tap water

Wash Water designations

WWU	Untreated wash water (pH = 13.0)
WW25T	25% CO_2-treated wash water (pH = 11.5)
WW50T	50% CO_2-treated wash water (pH = 10.0)
WW75T	75% CO_2-treated wash water (pH = 8.5)
WW100T	100% CO_2-treated wash water (pH = 7.0)
WWT0H	100% CO_2-treated wash water immediately after CO_2-treatment
WWT1H	100% CO_2-treated wash water 1 hour after CO_2-treatment
WWT3H	100% CO_2-treated wash water 3 hours after CO_2-treatment
WWT1D	100% CO_2-treated wash water 24 hours after CO_2-treatment
WWT3D	100% CO_2-treated wash water 72 hours after CO_2-treatment
WWT7D	100% CO_2-treated wash water 168 hours after CO_2-treatment

Mortar mixture designations (W/C = 0.485)

CTRL	Control mixture with regular tap water
WWU	100% tap water replacement with untreated wash water
WWUC	100% tap water replacement with untreated wash water and reduced cement content
WWT	100% tap water replacement with 100% CO_2-treated wash water
WWTC	100% tap water replacement with 100% CO_2-treated wash water and reduced cement content

Mortar mixture designations (W/C = 0.485) (continued)

WWT50	50% tap water replacement with 100% CO_2-treated wash water
WWT50C	50% tap water replacement with 100% CO_2-treated wash water and reduced cement content
WW50T	100% tap water replacement with 50% CO_2-treated wash water
WW50TC	100% tap water replacement with 50% CO_2-treated wash water and reduced cement content

Mortar mixture designations (W/C = 0.42)

CTRL-42	Control mixture with regular tap water
WWT-42	100% tap water replacement with 100% CO_2-treated wash water
WWTC-42	100% tap water replacement with 100% CO_2-treated wash water and reduced cement content

Mortar mixture designations (W/C = 0.55)

CTRL-55	Control mixture with regular tap water
WWT-55	100% tap water replacement with 100% CO_2-treated wash water
WWTC-55	100% tap water replacement with 100% CO_2-treated wash water and reduced cement content

Concrete mixture designations (W/C = 0.45)

CTRL	Control mixture with regular tap water
WWU50	50% tap water replacement with untreated wash water
WWU	100% tap water replacement with untreated wash water
WWT50	50% tap water replacement with 100% CO_2-treated wash water
WWT	100% tap water replacement with 100% CO_2-treated wash water
WWTC	100% tap water replacement with 100% CO_2-treated wash water and reduced cement content
WW50T	100% tap water replacement with 50% CO_2-treated wash water

Chapter 1. Introduction

1.1 Background Information

Concrete is the 'most abundant' and 'widely used building material', made by mixing hydraulic cement and aggregates with water (Koren and Hall 2002; Mehta and Monteiro 2006). The annual production of concrete, which is around 25 billion tonnes (roughly 11 billion cubic metres) per year, illustrates the importance of concrete (CSI 2009). Hydraulic cement has good adhesive properties and therefore it is used as a binder to produce concrete. However, the process of cement manufacturing is responsible for about 8% of the world's total CO_2 emissions and CO_2 is considered as the major contributor for climate change (Suhendro 2014). According to statistics, the estimated annual production of cement was around 4 billion tonnes in 2018 (CEMBUREAU 2019). This massive production rate creates significant environmental issues due to excessive CO_2 emissions.

In addition to that, discharge of wash water, also known as concrete wastewater, is another problem faced by the concrete industry. Wash water is the 'concrete wastewater' accumulated after cleaning concrete mixer trucks (Tran 2007). A huge amount of water is required for the cleaning and maintenance of concrete mixing trucks (Chini et al. 2001). Wash water is considered as a 'hazardous waste' and dumping of wash water in a landfill or into a water source without proper treatment of 'caustic materials' is prohibited as it produces considerable environmental impacts and health issues (Xuan et al. 2016; Vieira and Figueiredo 2016; EPA 2012). Hence, the disposal of wash water is often an arduous process for the concrete producers due to the complexity in the operational setup and the financial concerns (Parker and Slimak 1977).

Reuse of wash water to make fresh concrete is one of the effective solutions to handle this situation. Numerous research studies have been conducted to investigate the possibility of reusing wash water in concrete (Tran 2007). The positive outcomes of the studies encouraged the construction industry to consider the reuse of wash water in new concrete.

A major drawback of using untreated wash water is that it affects the fresh concrete properties, such as workability, and setting time (Lobo and Mullings 2003). Treating wash water with carbon dioxide (CO_2) may eliminate the negative effects. Concrete produced with CO_2-treated wash water has good fresh and hardened concrete properties compared with concrete produced with untreated wash water (MacDonald et al. 2020). Further studies are required to analyse various properties of carbonated wash water and the performance of concrete produced with CO_2-treated wash water.

1.2 Problem Statement

A massive quantity of water is being used to produce concrete and to clean concrete mixer trucks. According to NRMCA (2016) report, a typical cubic meter of concrete uses 130 litres of water for batching and requires a further 120 litres of water for cleaning. Since water is considered as one of the depleting natural resources of Earth, the overconsumption of potable water in ready-mixed concrete leads to unsustainability.

The cleaning process produces a large amount of wash water. Wash water cannot be discharged on the land as it generates environmental impacts. Therefore, concrete producers are struggling to manage and dispose of wash water economically.

Untreated wash water can be used to make concrete, but it affects the fresh concrete properties. Further research is required to find methods for alleviating the adverse effects of using wash water.

1.3 Research Scope and Limitations

The partial or complete replacement of potable water with CO_2-treated wash water would benefit the environment through resource management and CO_2 reduction. The CO_2 emitted from various industrial activities, especially cement manufacturing, can be used for the treatment of wash water. Recent studies disclosed the potentials of reusing CO_2-treated wash water for concrete mixes without affecting concrete properties and this proposed study would help to attain more in-depth knowledge on the subject.

This study is limited to wash water samples made entirely of Portland cement. But in practice, wash water produced in ready mix batching plants often consists of other materials, such as mineral and chemical admixtures, some amount of fine aggregate, and, in some cases, fibres. This variability of concrete wash water was not considered for this research.

Fresh concrete properties and hardened concrete properties of concrete specimens produced from various wash water mixes were investigated in this study. However, some durability parameters such as resistance to alkali-aggregate reactions (AAR), resistance to shrinkage cracking, and sulphate resistance were not examined. Freeze-thaw resistance of the concrete produced from wash water was evaluated.

1.4 Goals and Objectives

The overall goal of this study is to investigate the potential for using CO_2-treated wash water to produce fresh concrete without affecting fresh or hardened concrete properties.

The specific objectives of the study are as follows,

- To examine and compare the chemical properties of untreated and CO_2-treated wash water.
- To measure the compressive strength of mortar cubes produced with CO_2-treated wash water.
- To study the fresh and hardened properties of concrete produced with CO_2-treated wash water.
- To determine an appropriate level of CO_2-treatment for wash water.
- To identify the limitations of replacing potable water with CO_2-treated wash water.

1.5 Research Questions and Hypotheses

This proposed study is based on the following research questions:

Question 1: The main concern of using untreated wash water in concrete is that it affects the concrete properties. Would the carbonation process prevent the hydration of wash water and eliminate the negative effects of the untreated wash water?

Hypothesis 1: Since carbonation of untreated wash water converts the clinker compounds and hydration phases into calcium carbonate, the hydration of the wash water will be arrested. Hence, the negative effects in untreated wash water can be prevented.

Question 2: Can wash water with higher specific gravity (above 1.03) be used as mixing water without diluting it with tap water?

Hypothesis 2: Provided that the concrete properties are not affected, wash water samples with higher specific gravity values (exceeding the optional total suspended solids (TSS) limit of 50,000 ppm) can be used. Also, recent studies suggest that the solids in wash water have cementitious properties. Therefore, it is possible to use wash water with higher TSS content as mixing water in concrete.

1.6 Significance of the Research

The issue of producing large quantities of wash water from concrete plants has been taken into consideration over the past few decades from an environmental sustainability perspective. Usage of excessive water for concrete batching and maintenance is regarded as an overconsumption of a natural resource. There are studies focused on reusing wash water as mixing water in concrete. The studies concluded that the use of untreated wash water in concrete affects the fresh concrete properties, whereas recent studies identified the potentials of using CO_2-treated wash water in concrete.

Treating wash water with CO_2 and reusing the CO_2-treated wash water to make concrete not only eliminates the shortcomings in wash water, but also serves as an effective technique to capture tons of CO_2 produced as an industrial by-product, especially from cement manufacturing plants. However, further research studies are required to investigate the properties of concrete produced with CO_2-treated wash water.

Upon the completion of this research study, the results would help concrete producers in determining the optimum level of treatment and replacement level of potable water with CO_2-treated wash water. More information would be available on the fresh and hardened properties of concrete made with CO_2-treated wash water. If industrial CO_2 (produced during cement manufacturing) is used for the treatment process, cement manufacturers will have a direct advantage by not expelling the CO_2. The general public would also benefit as it leads to environmental sustainability.

1.7 Outline of the Thesis

This thesis is written in a way that provides the readers with adequate background information to understand this research study and its outcomes. This thesis is structured according to the 'traditional format' as outlined by the University of New Brunswick School of Graduate Studies and consists of 5 chapters. In Chapter 1, research background, problem statement, research goals and objectives, scope and limitation, research questions and hypotheses, and significance of this research are presented. Chapter 2 provides a comprehensive review of the relevant literature on the chemistry of cement and concrete, the durability of concrete, and the reuse of wash water as mixing water for concrete production. In Chapter 3, the materials used and test procedures followed for this study are described. Chapter 4 presents the results obtained during the course of this research programme along with extensive discussions of the results. Chapter 5 summarises the conclusions obtained from this study and recommendations for future research studies.

Chapter 2. Literature Review

2.1 Chemistry of Cement and Concrete

Concrete is a composite material made of hydraulic cement, aggregates, water, and chemical and/or mineral admixtures and these basic ingredients are known as 'concrete-making materials' (Popovics 1979). Portland cement is the dominant class of hydraulic cement used in concrete production. Tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF) typically make up more than 90% of the weight of Portland cement and are known as the 'major constituents of Portland cement clinker' (Kosmatka 2002). The mineral names and composition of the major constituents of Portland cement are presented in Table 2.1. In addition to these major constituents, other components such as sodium, potassium, magnesium, sulphate, phosphorus, and titanium are also commonly present in small quantities in Portland cement and these minor constituents are referred to as 'trace elements' (ACI 225R 1999).

Table 2.1 Major Constituents of Portland cement (Popovics 1979)

Name	Mineral Name	Abbreviation	Composition
Tricalcium silicate	Alite	C_3S	$3CaO.SiO_2$
Dicalcium silicate	Belite	C_2S	$2CaO.SiO_2$
Tricalcium aluminate	Aluminate	C_3A	$3CaO.Al_2O_3$
Tetracalcium aluminoferrite	Ferrite	C_4AF	$4CaO.Al_2O_3.Fe_2O_3$

The actual quantity of each compound depends on the type of cement and varies from cement to cement. Bogue's (1955) equations are generally used to calculate the weight percentages of all four major components of Portland cement (Neville 1987). C_3S and C_2S

are typically present in large quantities in Portland cement and comprise 40 to 63% and 9 to 31% (by weight) of Type GU Portland cement, respectively. The amounts of C_3A and C_4AF found in cement are relatively small and represent 6 to 14% and 5 to 13% of total weight of Type GU Portland cement, respectively (ACI 225R 1999). Gypsum ($CaSO_4.2H_2O$ or $C\underline{S}H_2$), typically about 5%, is also added to Portland cement to control the rate of hydration at early ages (Mindess et al. 2003).

2.2 Hydration of Cement

Hydraulic cement reacts with water and produces a strong, water-insoluble solid. Hydration of cement is a series of sequential chemical reactions that occurs approximately at the same time between the water and the cement particles. This process results in setting and hardening of cement paste (Popovics 1979).

Calcium silicates (both C_3S and C_2S) react with water and produce calcium silicate hydrate (C-S-H) (Kosmatka et al. 2002) as shown in Equations 2.1. and 2.2. The hydration of C_3S is controlled by the rate of diffusion whereas hydration of C_2S is controlled by its slow intrinsic rate of reaction (Lea 1960). As a result, C_3S and C_2S have a different rate of hydration and C_2S reacts more slowly than C_3S (Neville 1987; Mindess et al. 2003). C-S-H consists of 50 to 60% of the total volume of hydration products and is recognised as the most important cementing component in concrete as it is predominantly responsible for the strength development of concrete (Tran 2007; Mehta and Monteiro 2006). Figure 2.1 depicts the relative volumes of each hydrating product over time.

The symbol C-S-H is generally used to denote calcium silicate hydrate since there is no exact stoichiometric composition. The C/S ratio varies between 1.5 and 2.0 and the bound water content (H) also varies significantly (Mindess et al. 2003).

$$2(3CaO.SiO_2) + 11H_2O \rightarrow 3CaO.2SiO_2.8H_2O + 3Ca(OH)_2$$

Equation 2.1

$$[2C_3S + 11H \rightarrow 3C\text{-}S\text{-}H + 3CH]$$

$$2(2CaO.SiO_2) + 9H_2O \rightarrow 3CaO.2SiO_2.8H_2O + Ca(OH)_2$$

Equation 2.2

$$[2C_2S + 9H \rightarrow 3C\text{-}S\text{-}H + CH]$$

In the absence of gypsum, C_3A violently reacts with water and causes undesirable rapid hardening of the cement paste, referred to as 'flash set'. Due to this reason, some form of calcium sulphate (typically gypsum) is always incorporated in cement to prevent the flash set (Mindess et al. 2003). The sequence of reactions is shown in Equations 2.3 to 2.5 (Kosmatka et al. 2002). Initially, C_3A reacts with water and gypsum to form ettringite (calcium sulfoaluminate or AFt) as shown in Equation 2.3, and then the remaining C_3A and water react with ettringite to produce stable calcium monosulfoaluminate (AFm) as shown in Equation 2.4. Any excess C_3A reacts with water and CH to produce tetracalcium aluminate hydrate (Equation 2.5).

$$3CaO.Al_2O_3 + 26H_2O + 3(CaSO_4.2H_2O) \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$$

Equation 2.3

$$[C_3A + 26H + 3C\underline{S}H_2 \rightarrow C_6A\underline{S}_3H_{32}]$$

$$2(3CaO.Al_2O_3) + 4H_2O + 3CaO.Al_2O_3.3CaSO_4.32H_2O \rightarrow 3(3CaO.Al_2O_3.CaSO_4.12H_2O)$$

Equation 2.4

$$[2C_3A + 4H + C_6A\underline{S}_3H_{32}) \rightarrow 3C_4A\underline{S}H_{12}]$$

$$3CaO.Al_2O_3 + 12H_2O + Ca(OH)_2 \rightarrow 3CaO.Al_2O_3.Ca(OH)_2.12H_2O$$

Equation 2.5

$$[C_3A + 12H + CH \rightarrow C_4AH_{13}]$$

The reaction of C_4AF with water is similar to C_3A except that it produces less heat of hydration and does not cause flash set (Mindess et al. 2003). C_4AF reacts with water and CH and produces calcium aluminoferrite hydrate (Kosmatka et al. 2002) as shown in Equation 2.6.

$$4CaO.Al_2O_3.Fe_2O_3 + 10H_2O + 2Ca(OH)_2 \rightarrow 6CaO.Al_2O_3.\ Fe_2O_3.12H_2O$$

Equation 2.6

$$[C_4AF + 10H + 2CH \rightarrow C_6AFH_{12}]$$

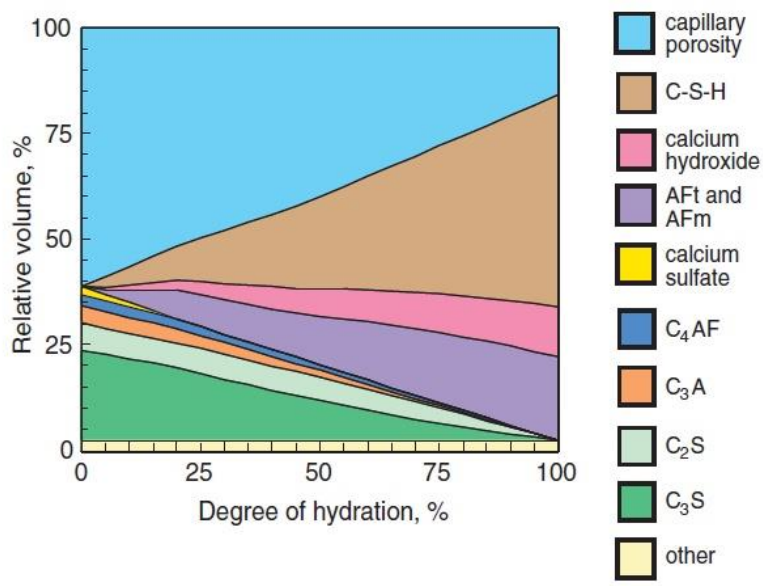

Figure 2.1 Relative Volumes of Major Compounds of Hydrating Portland Cement as a Function of the Degree of Hydration (Kosmatka et al. 2002)

2.3 Setting Time

A freshly mixed concrete is typically in a plastic or semi-fluid state and becomes solid when the concrete hardens. The term 'setting' is used to describe the stiffness of concrete

paste (Neville 1987). Setting time of concrete refers to the time required for the 'stiffening' of cement paste to a certain degree of consistency and two 'arbitrarily chosen points' are used to describe the stages of setting as illustrated in Figure 2.2 (Mindess et al. 2003; Neville 1987). The initial setting time of concrete refers to the time in which the cement paste begins to harden, and the final setting time is the time when the cement paste is sufficiently hardened to carry some load (Naik et al. 2001; Mindess et al. 2003).

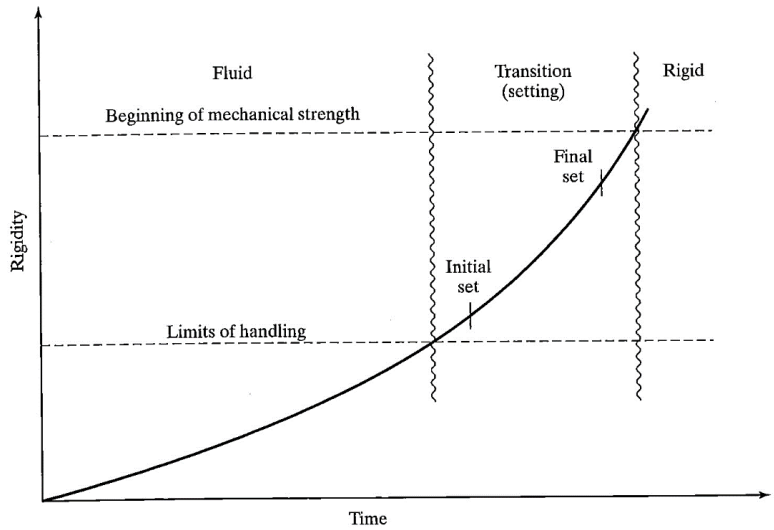

Figure 2.2 The Process of Setting and Hardening of Concrete Paste (Mindess et al. 2003)

2.4 Heat of Hydration

The hydration of cement compounds is exothermic and up to 500 J of heat energy is released per 1 gram of cement during hydration (Neville 1987). The heat of hydration varies significantly with the cement composition and the rate of heat evolution depends on the degree of fineness of the cement (Mindess et al. 2003). The relationship between the rate of heat evolution and time is shown in Figure 2.3.

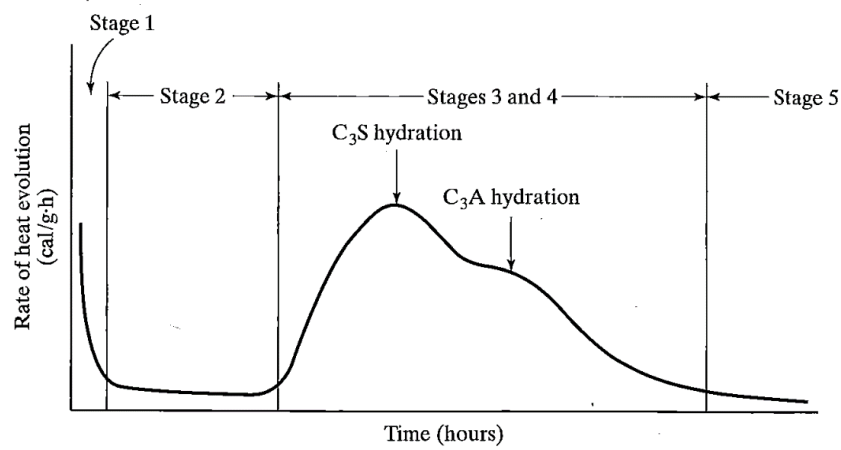

Figure 2.3 Rate of Heat Evolution During Hydration of Portland Cement (Mindess et al. 2003)

Stage 1, which is the 'initial stage' of contact between cement and water, refers to the initial hydrolysis of C_3A and C_3S. Stage 2 is known as 'dormant period' and corresponds to the initial set of cement paste. Accelerated reaction of hydration products occurs during Stage 3 (referred to as 'acceleration period') and the rate of hardening and final set is determined at this stage. Stage 4, known as 'deceleration period', decelerates the formation of hydrated products and determines the rate of early strength gain. Stage 5 corresponds to the steady formation of hydration products and is referred to as the 'steady state' (Kosmatka et al. 2002; Mindess et a. 2003).

2.5 Types of Cement

There are several types of cement available for the production of concrete. Portland cement and other modified versions of Portland cement are the major hydraulic cements used today (Mehta and Monteiro 2006). Each type of cement has different chemical compositions and properties. The major types of Portland cement and their typical chemical composition and properties are presented in Table 2.2 and Table 2.3, respectively.

Table 2.2 Types of Portland Cement (ASTM C150 2019; CSA A3001 2003)

Description	ASTM C150	Equivalent CSA A3001
General use	I	GU
Moderate sulphate resistance or moderate heat of hydration	II	MS or MH
High early strength	III	HE
Low heat of hydration	IV	LH
High sulphate resistance	V	HS

Table 2.3 Typical Chemical Composition and Properties of Portland Cements (Adapted from Mindess et al. 2003)

Type	I	II	III	IV	V
C_3S (%)	55	55	55	42	55
C_2S (%)	18	19	17	32	22
C_3A (%)	10	6	10	4	4
C_4AF (%)	8	11	8	15	12
$C\underline{S}H_2$ (%)	6	5	6	4	4
Blaine fineness (m^2/kg)	365	375	550	340	380
Compressive strength (1-day)	15	14	24	4	12
Heat of hydration (7-day, J/g)	350	265	370	235	310

2.6 Supplementary Cementitious Materials (SCMs)

Portland cements are often partially replaced by supplementary cementitious materials (SCMs), such as slag, fly ash, silica fume, and other pozzolans, to enhance fresh and/or hardened properties of concrete without affecting the quality of the concrete (Thomas 2013; Mindess et al. 2003). SCMs are also known as mineral admixtures. One or more

SCMs can be mixed with Portland cement to make blended cements. The SCMs are often waste products or by-products of other industrial processes (Kosmatka et al. 2002). The appropriate use of SCMs also improves the durability of concrete, especially in harsh environments (Thomas 2013). Therefore, the SCMs are widely incorporated in concrete production.

2.7 Chemical Admixtures

Chemical admixtures are special chemical ingredients added to the concrete before or during the mixing process (Kosmatka et al. 2002). Chemical admixtures can be used to modify certain properties of concrete or to achieve desirable properties economically which cannot be accomplished by any other method (Popovics 1979). There are several types of chemical admixtures used in concrete, such as set-time controlling admixtures, water-reducing admixtures, and air-entraining admixtures. But only two types of chemical admixtures (air-entraining admixture and high-range water-reducers), which were used for this research study, are elaborated in this chapter.

2.8 Air-Entraining Admixture

The durability of concrete in a freezing and thawing environment can be improved by incorporating a proper air-void system in concrete and this can be achieved by adding air-entraining admixtures to the concrete (ASTM C260 2016; Mindess et al. 2003). Air-entraining admixtures are made with surface-active chemicals, which generally consist of salts of wood resin, proteinaceous materials and petroleum acids, and some synthetic detergents (Mehta and Monteiro 2006). In the absence of AEA the bubbles that are created

by the mixing process coalesce and exit the concrete due to buoyancy. AEA stabilize the bubbles introduced during mixing by making the air bubbles firmly attached to the cement particles in concrete. The molecules of surface-active chemicals (surfactants) have both hydrophobic and hydrophilic portions. The hydrophobic portion of the molecules orients towards the air bubbles at the air-water interfaces, whereas the polar groups align towards the water phase. As a result, the water surface tension decreases and facilitates air bubble formation. Moreover, the polar groups attach to the solid phases (i.e. cement particles) and displace the water so that the air bubbles remain attached with the cement particles (Popovics 1979; Mehta and Monteiro 2006). This mechanism is graphically illustrated by Figure 2.4. The mechanism of air-entrainment in providing freeze-thaw protection is discussed in Section 2.12.2.

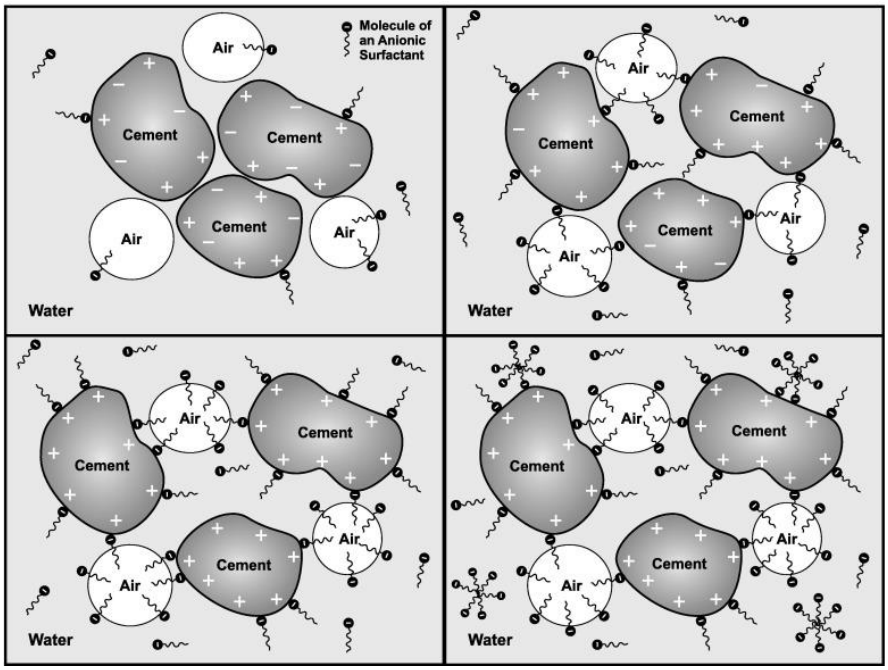

Figure 2.4 Mechanism of Air-Entrainment in Concrete (Mendes et al. 2017)

2.9 High-Range Water-Reducers (HRWR)

A water-reducing admixture can be defined as a material that significantly reduces the amount of mixing water required to produce concrete with a certain degree of consistency (Mehta and Monteiro 2006). High-range water-reducers (HRWR) are also known as 'superplasticisers'. Superplasticisers greatly curtail the water demand and make concrete with low water-cement ratios more workable. Superplasticisers typically consist of chemicals such as sulfonated melamine formaldehyde condensates, sulfonated naphthalene formaldehyde condensates, lignosulfonates, and polycarboxylates (Kosmatka et al. 2002). Water-reducers work by being adsorbed on the surface of cement particles and producing a negative charge that makes the particles disperse. This stabilized dispersion reduces the interfacial tension. The particles become more mobile and consequently the concrete workability greatly increases (Neville 1987; Popovics 1979). With the use superplasticisers, the water content to achieve a specific workability can be reduced by as much as 35% (Neville 1987). Figure 2.5 presents the relationship between the flow (workability) and water content of concrete with or without the use of superplasticiser.

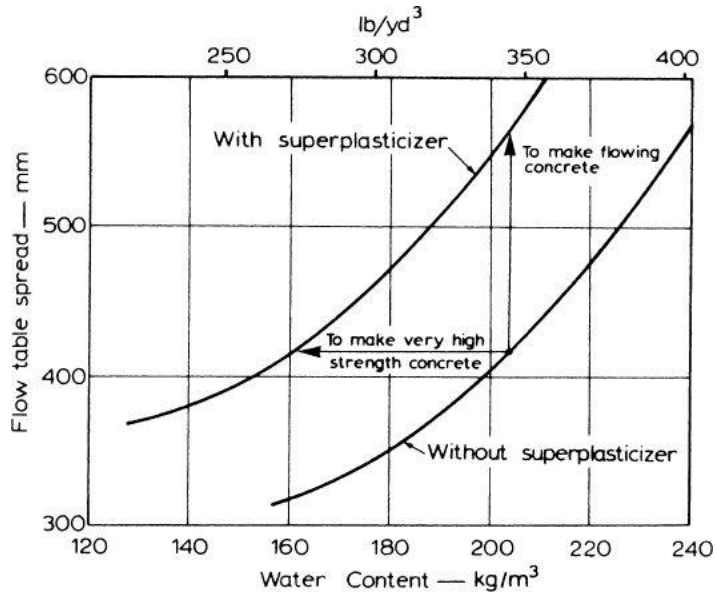

Figure 2.5 Effect of Superplasticiser on Flow of Concrete (Neville 1987)

2.10 W/CM Ratio

The ratio of water-to-cement (W/C) is a simple mathematical relationship between the quantity of mixing water and cement, which is the ratio of the mass of mixing water to the mass of cement. This relationship (W/C ratio) can be given by the following equation (Equation 2.7):

$$W/C = \frac{mass\ of\ mixing\ water}{mass\ of\ cement}$$ **Equation 2.7**

Abrams (1918) expressed the relationship between the water-to-cement (W/C) ratio and the strength of concrete in 1918 using an empirical formula (Equation 2.8).

$$f_c = \frac{K_1}{K_2{}^{(w/c)}}$$ **Equation 2.8**

Where, w/c – water/cement ratio of the concrete mixture, and k_1, k_2 – empirical constants.

According to the equation, the strength of concrete is inversely proportional to the water-to-cement (W/C) ratio. This relationship between the compressive strength and W/C ratio of concrete is shown in Figure 2.6. The shaded area (blue) in Figure 2.6 represents the 28-day compressive strengths of more than 100 different non-air-entrained Portland cement concrete mixtures that were cast between 1985 and 1999 (Kosmatka et al. 2002). Water-to-cementitious-material (W/CM) ratio is generally preferred over W/C today because of the wide use of SCM. In this ratio, CM represents the mass of all cementitious materials (Portland cement plus SCM).

The strength development of concrete depends on the degree of hydration. Concrete gains strength when enough water is available for hydration. A minimum W/CM ratio of 0.38 is required to achieve complete hydration (Powers 1958). The W/CM ratio plays a significant role in attaining the required fresh and hardened properties of concrete. Therefore, W/CM is considered a fundamental parameter in the design of concrete mixture.

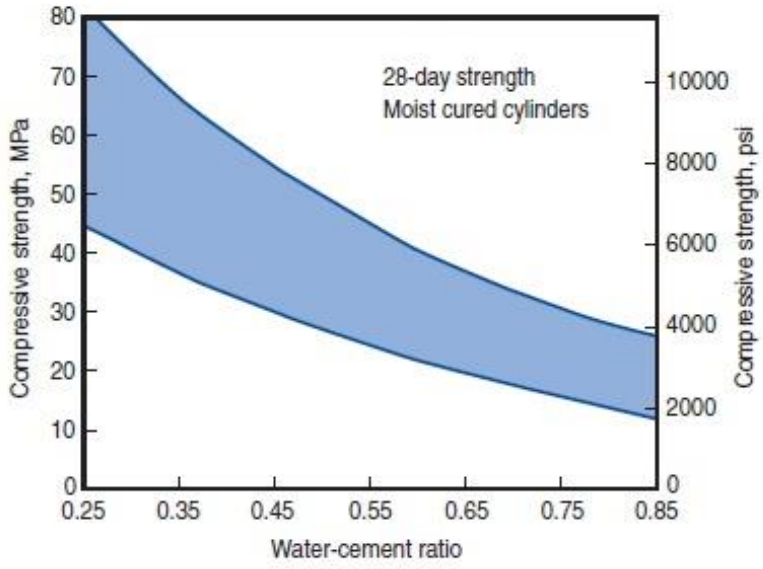

Figure 2.6 The Relationship Between the Compressive Strength of Concrete and The W/C Ratio (Kosmatka et al. 2002)

2.11 Strength of Concrete

The strength of a material is defined as its ability to withstand stress without failure. Similarly, the strength of concrete can be defined as the maximum stress that concrete can withstand (Mehta and Monteiro 2006). The strength of concrete is often used to describe the quality of the concrete. For a given combination of cementing materials, the two major factors governing the strength of concrete are water-to-cementing-materials (W/CM) ratio and the degree of compaction. This is graphically illustrated in Figure 2.7. The compressive strength of concrete is inversely proportional to its W/CM ratio. Moreover, the type of compaction (degree of compaction) also affects the compressive strength of concrete. Fully compacted concrete achieves a higher compressive strength compared to insufficiently compacted concrete.

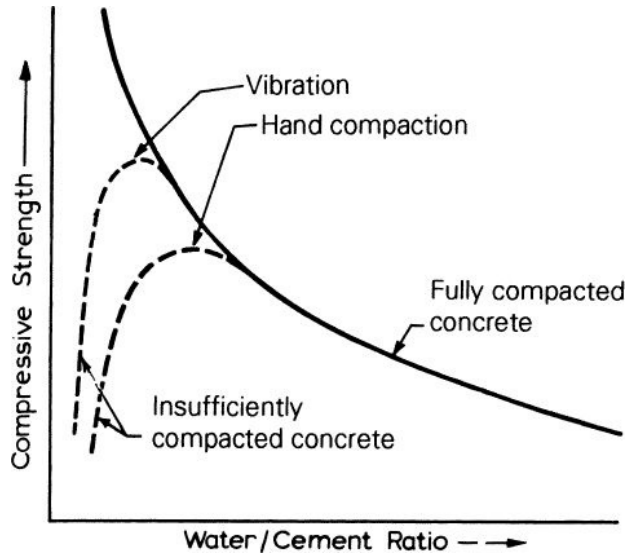

Figure 2.7 Influence of W/C Ratio and Compaction on Compressive Strength (Neville 1987)

Similar to W/CM ratio, porosity of concrete also has an inverse relationship to the strength of concrete. The strength-porosity relationship can be expressed for homogeneous materials, including concrete, as in Equation 2.9 (Mehta and Monteiro 2006).

$$S = S_0 e^{-kp}$$ **Equation 2.9**

Where, S – Strength of the materials, S_0 – intrinsic strength at zero porosity, k – constant, and p – porosity of the given material.

The above relationship clearly demonstrates that when the pore volume of concrete is minimal, concrete tends to achieve high strength. This emphasises the importance of proper curing and the availability of moisture to complete the hydration of cement paste to reduce the porosity of concrete. Figure 2.8 illustrates the effect of curing on strength development of concrete. This implies that the strength development of concrete is proportional to the curing period.

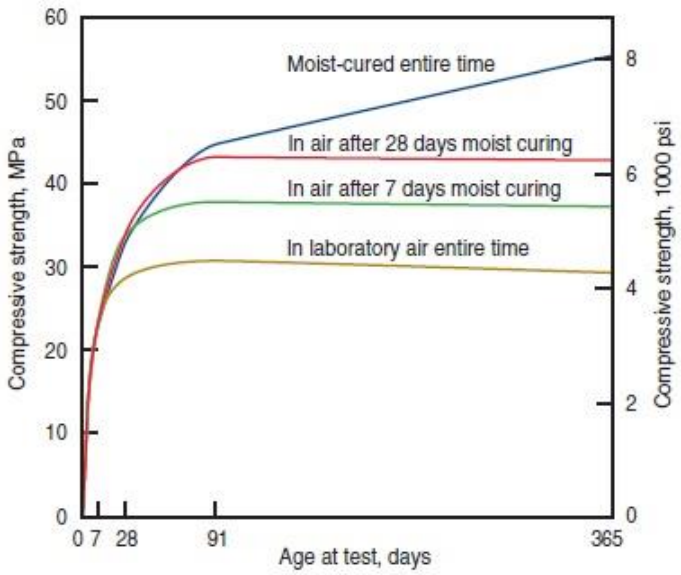

Figure 2.8 Effect of Curing on Strength Development of Concrete (Kosmatka et al. 2002)

Testing of concrete strength in the laboratory is relatively easy compared to durability tests for concrete. Two major strengths are considered for concrete and they are compressive strength and tensile strength. Concrete is relatively strong under compression and weak in tension. Since the direct tension testing for concrete is a complicated test method, flexural strength tests (termed the modulus of rupture) and spitting tensile strength tests are often preferred to evaluate the performance of concrete under tension (Neville 1987). The relationship between the compressive strength of concrete and the flexural strength of concrete (modulus of rupture) is given by the following equation (Equation 2.10) (Wood 1992):

$$f_r = 0.7\sqrt{f_c}$$ **Equation 2.10**

Where, f_r – modulus of rupture (MPa), f_c – compressive strength (MPa).

A similar relationship (Equation 2.11) can also be expressed between the compressive strength of concrete and the splitting tensile strength of concrete (ACI 318R 2014).

$$f_{st} = 0.56\sqrt{f_c}$$ **Equation 2.11**

Where, f_{st} – splitting tensile strength (MPa), f_c – compressive strength (MPa).

Neville (1987) stated that the nature of aggregates may also affect the ratio of the tensile strength (f_t) to the compressive strength (f_c).

2.12 Durability of Concrete

Durability is the most crucial property for any concrete (ACI 201.2R 2008). Kosmatka et al. (2002) defined the durability of concrete as 'the ability of concrete to resist weathering action, chemical attack, and abrasion while maintaining the desired engineering properties'. Concrete is considered to be durable if it withstands the conditions of the intended service environment without deterioration throughout its designed service-life (Neville 1987). Water-to-cementitious materials (W/CM) ratio is an important parameter that influences the durability of concrete (Mindess et al. 2003). The type of binder in terms of type and level of SCM is also critical in determining durability (Thomas 2013).

Shrinkage cracking, freezing and thawing damage, corrosion of embedded steel in concrete, sulphate attack, delayed ettringite formation (DEF), and alkali-aggregate reactions (AAR) are the most common types of concrete deterioration. Design of durable concrete is of great significance in terms of safety and life-cycle costs.

2.12.1 Resistivity of Concrete

Chloride ingress is a serious concern for reinforced concrete structures as it may lead to the corrosion of embedded steel. Hence, structural concrete should have a tolerable resistance to inhibit the chloride ions from reaching the rebar. Concrete resistivity tests are electrical tests that measure either the electrical conductivity or resistivity of concrete which has been found to provide a reasonable surrogate for mass transport properties such as chloride ingress (Azarsa and Gupta 2017; Layssi, et al. 2015). ASTM C1202 (2019) is commonly used to evaluate the concrete's ability to resist chloride ion penetration. But this method is neither quick nor simple (Layssi, et al. 2015). Researchers have focused on developing alternate testing methods to overcome these drawbacks associated with ASTM C1202 and have identified electrical resistivity as a potential alternative (Azarsa and Gupta 2017).

Electrical resistivity tests are non-destructive techniques (NDT) and the sample preparation and experimental setup are much more convenient and quicker than ASTM C1202 (Layssi et al. 2015). Two methods for measuring electrical resistivity were used in this study; these were (i) the bulk resistivity tests and (ii) the surface resistivity test.

The bulk resistivity test method (ASTM C1876) is generally used to measure the electrical resistivity of concrete specimens. But, over the last decade, surface resistivity method (AASHTO T358 2015) has gained a great deal of attention as it provides promising in-situ results leading to a good indication of mass-transport properties of concrete when an appropriate correction factor is applied (ASTM WK37880 2013). Figure 2.9 and Figure

2.10 present the schematic diagrams of the bulk and surface resistivity test methods, respectively.

Ohm's law is used to measure the resistance across the concrete specimens. Equation 2.12 shows the formula for Ohm's law.

$$V = IR \rightarrow R = \frac{V}{I}$$ **Equation 2.12**

Where, V – potential difference (V), I – current (A), and R – resistance (Ω).

Resistance (R) depends on the material properties and the dimensions of the material and can be expressed as a function of the material and specimen dimension. In contrast, resistivity (ρ) is an inherent material property that is independent of dimensions (Layssi et al. 2015). Equation 2.13 shows the relationship between the resistance (R) and resistivity (ρ). Both resistance (R) and resistivity (ρ) are functions of the degree of saturation of the concrete (Azarsa and Gupta 2017) and meaningful results can only be obtained if the concrete is fully saturated prior to measurement.

$$R = \rho \frac{L}{A} \rightarrow \rho = R \frac{A}{L}$$ **Equation 2.13**

Where, R – resistance (Ω), A – cross-sectional area (m^2), L – length (m), and ρ – resistivity (Ω.m).

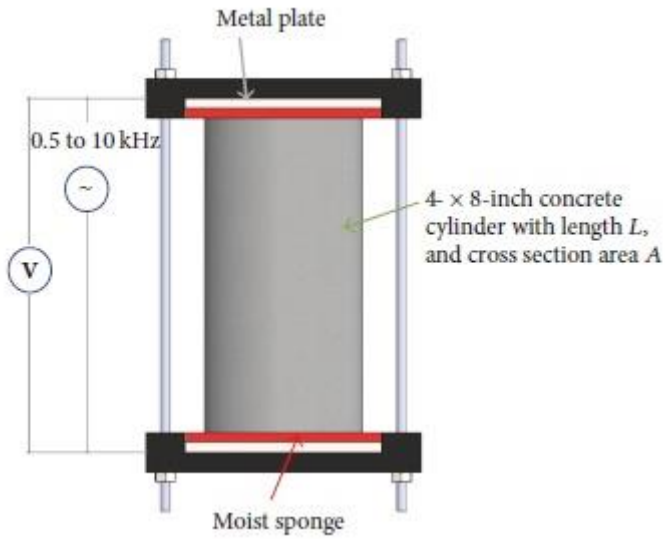

Figure 2.9 Schematic Diagram of the Bulk Resistivity Test Method (Azarsa and Gupta 2017)

The surface resistivity test method uses the principle of Wenner four-point array probe (Layssi et al. 2015). Equation 2.14 shows the formula associated with the Wenner four-point array probe.

$$\rho = 2\pi a \frac{V}{I}$$ **Equation 2.14**

Where, ρ – resistivity (Ω.m), a – spacing of the probe (m), V – potential difference (V), and I – current (A).

Although this is a simple and useful technique for measuring the surface resistivity of concrete, the Wenner method is more suitable for large and flat specimens. Since the length of cylindrical concrete specimens is typically only a few times higher than the electrode spacing of Wenner probe, the measured surface resistivity value is often higher than the actual surface resistivity of the concrete specimen. Therefore, a geometric correction should be applied to determine the true surface resistivity of concrete. The geometric

correction factor is a function of the geometry and dimensions of the concrete specimen and the electrode spacing. For the concrete specimens having the dimensions of 100 mm (diameter) x 200 mm (length) the geometric correction factor is (1/1.95) if the electrode spacing is 38 mm (ASTM WK37880 2013).

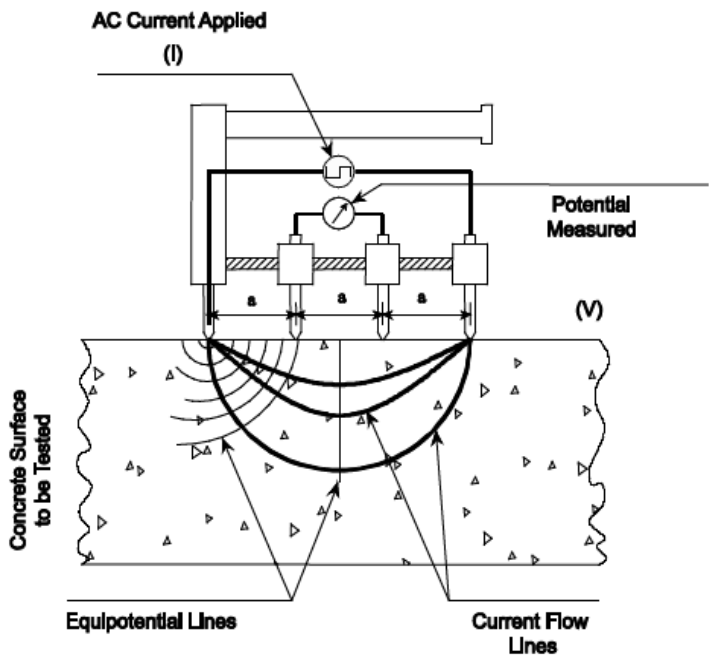

Figure 2.10 Schematic Diagram of Wenner Four-Point Array Probe Test Setup (AASHTO T358 2015)

2.12.2 Freeze-Thaw Resistance of Concrete

One of the most destructive weathering factors for concrete is freezing and thawing (Kosmatka et al. 2002). Non-air-entrained concrete exposed to a freeze-thaw environment has the potential to be damaged. Freezing and thawing damage is also referred to as 'frost attack'. Resistance to freezing and thawing is of great importance in countries with extremely colder temperatures, including Canada and certain parts of the United States of America.

The volume of water increases by about 9% when it freezes. When water freezes in the voids of moist concrete, it exerts hydraulic pressure on the surrounding cement paste and aggregates and eventually develops osmotic pressure due to the concentration gradient of the dissolved ions in the pore solutions. As the freeze-thaw cycles repeat, it causes scaling and cracking of concrete. Concrete also loses its stiffness and strength when exposed to cyclic freezing and thawing (Shang et al. 2013). Figure 2.11 shows the appearance of both non-air-entrained and air-entrained concrete specimens after being subjected to 150 freeze-thaw cycles. It can be noticed that the concrete produced without air-entrainment exhibited severe damages compared to air-entrained concrete. Furthermore, concrete structures that are already damaged by freezing and thawing are most vulnerable to corrosion when the concrete is exposed to de-icing salts (Kosmatka et al. 2002).

Figure 2.11 Non-Air-Entrained Concrete and Air-Entrained Concrete After 150 Freeze-Thaw Cycles (Kosmatka et al. 2002)

Entrained air in concrete serves to lessen the pressure exerted as a result of the freezing and thawing, assuming that the air-void system consists of well-distributed entrained air with adequate bubble sizes (Tran 2007). Figure 2.12 graphically illustrates the effectiveness of air-entrainment in preventing the freeze-thaw damage. CSA A23.1 (2014) specifies an air content of 5-8% for concrete exposed to a severe freezing and thawing environment. This can be achieved with the help of an air-entraining admixture.

Concrete made with frost-susceptible aggregates is also vulnerable to frost attack, even with adequate air-entrainment (ACI 201.2R 2008). Therefore, it is necessary to use frost-resistant aggregates in concrete along with an effective entrained air-void system to protect against freezing and thawing damage.

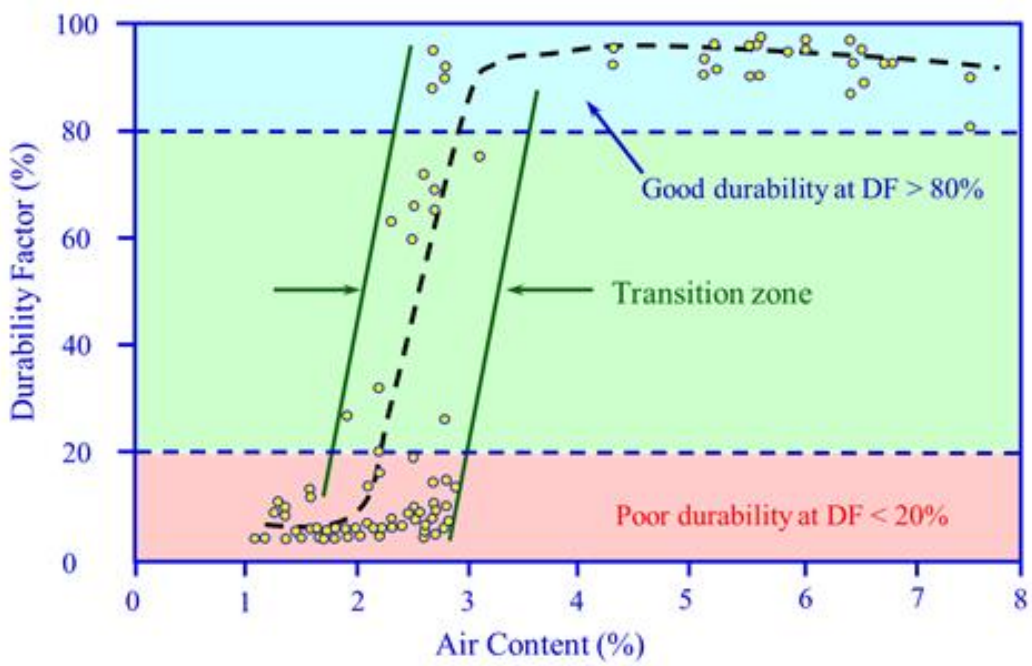

Figure 2.12 Effect of Air-Entrainment on Resistance to Freeze-Thaw Damage (Thomas 2019; Newlon and Mitchell 1994)

2.13 Mixing Water

Water is one of the fundamental concrete-making materials. Any potable water is suitable for concrete making, and non-potable water can also be used as mixing water as long as it complies with the requirements for mixing water (Table 2.4 and Table 2.5) outlined in ASTM C1602 (2018).

Table 2.4 presents the prescriptive requirements for mixing water and any water that satisfies these limits can be used as mixing water. However, even water outside of these limits may be used as mixing water if it meets the strength and setting time requirements of Table 2.5 when tested in mortar.

Table 2.4 Chemical Limits for Mixing Water (ASTM C1602 2018)

	Limits (ppm)	Test Method
Chloride (as Cl^-)		
Prestressed concrete or concrete in bridge decks	500	C114
Other reinforced concrete	1,000	C114
Sulphate (as SO_4^{2-})	3,000	C114
Alkalis (as $Na_20 + 0.658\ K_20$)	600	C114
Total solids (by mass)	50,000	C1603

Table 2.5 Performance Requirements for Mixing Water (ASTM 1602 2018)

	Limits
Compressive strength, minimum percentage of control at 7 days	90
Time of setting, deviation from control (h:min)	From 1:00 earlier to 1:30 later

2.14 Workability

The workability of concrete broadly refers to the 'consistency and cohesiveness' of a concrete mixture and can be defined as 'the property that determines the ease of placement, compaction, and finishing of concrete without segregation' (Mehta and Monteiro 2006). Consistency of a concrete mixture, which describes the ease of flow, is often measured by the slump-cone test. Figure 2.13 shows the typical types of slump of concrete and they are: (i) true slump, (ii) shear slump, and (iii) collapse slump. Workability is considered to be a key property as it affects constructability.

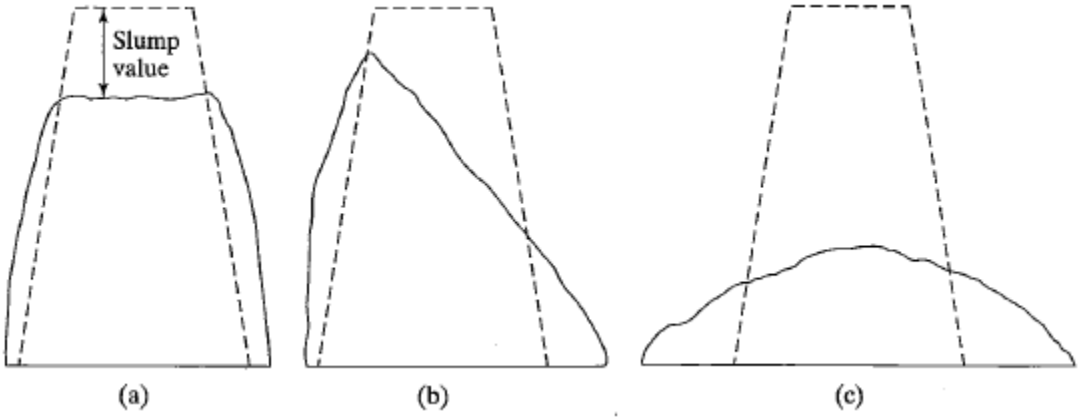

Figure 2.13 Types of Slump (a) True Slump, (b) Shear Slump, and (c) Collapse Slump (Mindess et al. 2003)

2.15 Thermal Analysis

Cement paste contains both physically and chemically bound water. Chemically bound water is firmly attached to the crystal phase and can only be separated by heating to a high temperature at a controlled rate or by chemical reactions (Prochoń and Piotrowski 2016). Therefore, measuring the chemically bound water requires a systematic approach of

thermal analysis. All bound water will be released when cement paste is heated to a temperature of 1,000 ºC due to the decomposition of the compounds in the cement paste (Fagerlund 2009; Hager 2013; Prochoń and Piotrowski 2016).

Thermogravimetric analysis (TGA) is extensively used for the purpose of measuring chemically bound water in hydrated cement or cement paste. This method uses the mass loss that occurs within a specific temperature range to quantify the bound water content.

Tran (2007) suggested that the TGA can be used to analyse the hydration of wash water samples. Matos et al. (2020) performed TGA on paste samples with 0, 50, and 100% wash water replacement levels. Chemically bound water (CBW) content and the amount of decomposed calcium hydroxide (CH) were measured in that study. These concepts are used in this study to investigate changes in chemically bound water over time and to quantify calcium hydroxide (CH) contents of wash water specimens. An example of thermogram obtained for a wash water specimen is shown in Figure 2.14.

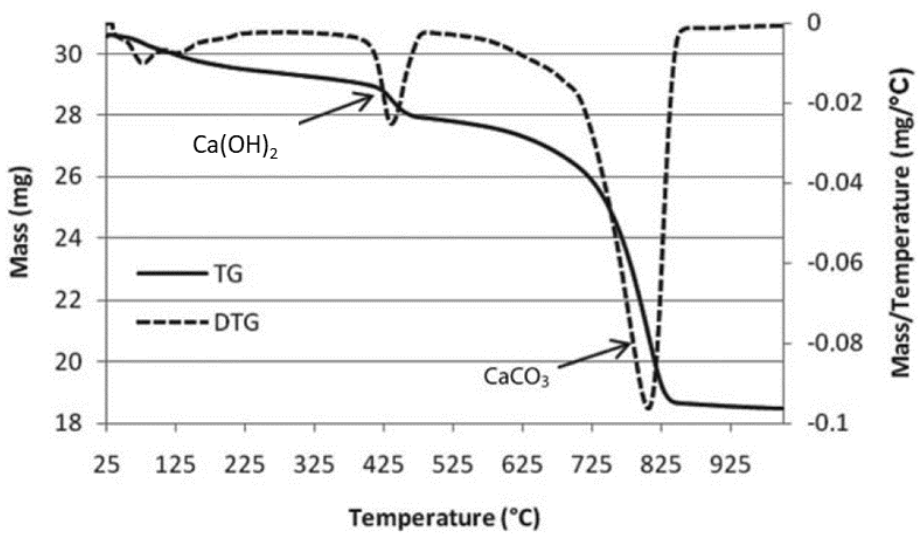

Figure 2.14 Thermogram Obtained for a Wash Water Specimen (Tsimas and Zervaki 2010)

2.16 X-Ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis is one of the powerful techniques used in qualitative and quantitative characterization of poly-phase materials (Kohli et al. 2015; Chatterjee 2001). X-rays are electromagnetic radiations of high energy and very short wavelengths (less than 100 angstroms) that can pass through most of the materials (Rendell 2002). X-ray diffraction is the elastic scattering of X-ray photons by atoms in a periodic lattice, and the XRD analysis has also turned out to be a virtually crucial tool to analyse cement and concrete materials (Chatterjee 2001). XRD analysis is useful in cement chemistry and provides more reliable quantification of the crystalline phases present in Portland cement (ACI 225R 1999).

Some researchers (MacDonald et al. 2020; Xuan et al. 2016; Tsimas et al. 2010) used the XRD method to track changes in chemical compositions of wash water specimens to analyse the hydration of wash water over time. Changes in calcium silicate phases (both C_3S and C_2S) and hydration products (such as C-S-H, CH, and ettringite) are indicative of ongoing hydration of cement paste or wash water specimens. The effect of carbonation on phase compositions of wash water can be seen in Figure 2.15. The phases present before carbonation include calcium silicates (both C_3S and C_2S), silicate (S), calcium aluminosilicate, and portlandite (CH), whereas after carbonation the phases are mainly calcium carbonate (C$\underline{C}$) and silicate (S).

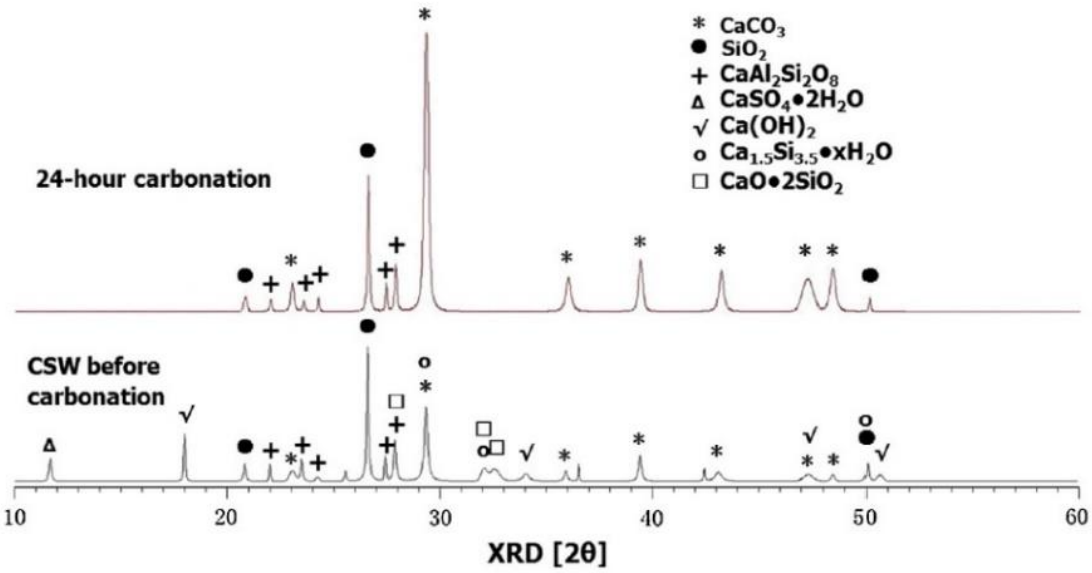

Figure 2.15 X-Ray Diffractograms Obtained Before and After The Carbonation of Wash Water (Xuan et al. 2016)

2.17 Concrete Wash Water

An enormous quantity of wash water is generated in concrete batching plants from washing trucks and equipment used for concreting works (Chini et al. 2001). The National Ready Mixed Concrete Association (NRMCA) stated that the production of a typical cubic metre of concrete uses 130 litres of water for batching and requires 120 litres of water for cleaning. Wash water has a high pH level (typically above 11.5) and it is classified as a 'corrosive hazardous waste' in many countries due to its alkaline characteristic (Tsimas and Zervaki 2001). Discharge of untreated wash water in landfills pollutes the environment and affects the ecosystem (Xuan et al. 2016). Caustic wash water is harmful to aquatic life and human skin (EPA 2012).

Concrete producers have to use a system to filter the hazardous materials or to neutralise wash water before efflux of wash water because of the strict environmental regulations.

Settling ponds are often used to separate the water from the solids (Parker and Slimak 1977) after which the water can be neutralized and discharged. However, MacDonald et al. (2020) emphasised that ready-mix concrete plants are still struggling to manage and dispose of wash water economically. Figure 2.16 depicts the schematic of a typical wash water reclamation system. A typical wash water reclamation system generally consists of a sedimentation tank and a filtration system. Coarse particles (i.e. aggregates) may be recovered from or before the sedimentation tank. Filtered wash water can be used as mixing water. Wash water obtained from the sedimentation tanks should be neutralised prior to discharge if it is not used as mixing water.

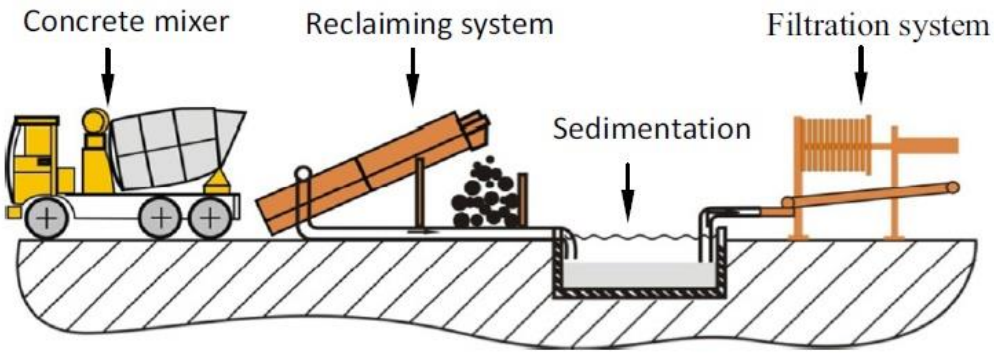

Figure 2.16 Wash Water Reclamation System (Xuan et al. 2016)

2.18 Use of Wash Water for Concrete Production

Current status of water scarcity around the world urges the need to find alternative water sources to use in concrete production. A potential strategy on hand is to practice beneficial reuse of wash water (Sandrolini and Franzoni 2001). This approach is an effective solution for the handling of wash water and it would significantly reduce the amount of freshwater consumption for concrete production.

While it is accepted as a proper solution, there are some limitations of using wash water for fresh concrete mixes (Su et al. 2000). Mainly, the use of wash water has an adverse effect on the setting time and workability of concrete (Borger et al. 1994; Matos et al. 2020). Borger et al. (1994) stated that construction companies were reluctant to use the concrete produced with recycled wash water for structural applications due to the limited availability of comprehensive research on this theme. CO_2-treatment was introduced to prevail over these deficiencies in untreated wash water. Carbonated wash water not only sustains the fresh concrete properties but also improves the compressive strength of concrete (MacDonald et al. 2020). According to ASTM C1602 (2018), a total suspended solids (TSS) content of less than 50,000 ppm is recommended for mixing water. The specific gravity of mixing water that satisfies this limit is approximately 1.03 (see Figure 2.17) (Lobo and Mullings 2003). Wash water with higher specific gravities can be diluted with regular water to achieve this requirement (MacDonald et al. 2020). However, wash water with a higher level of TSS content is permitted provided that it satisfies the performance requirements (mortar testing) outlined in Table 2.5.

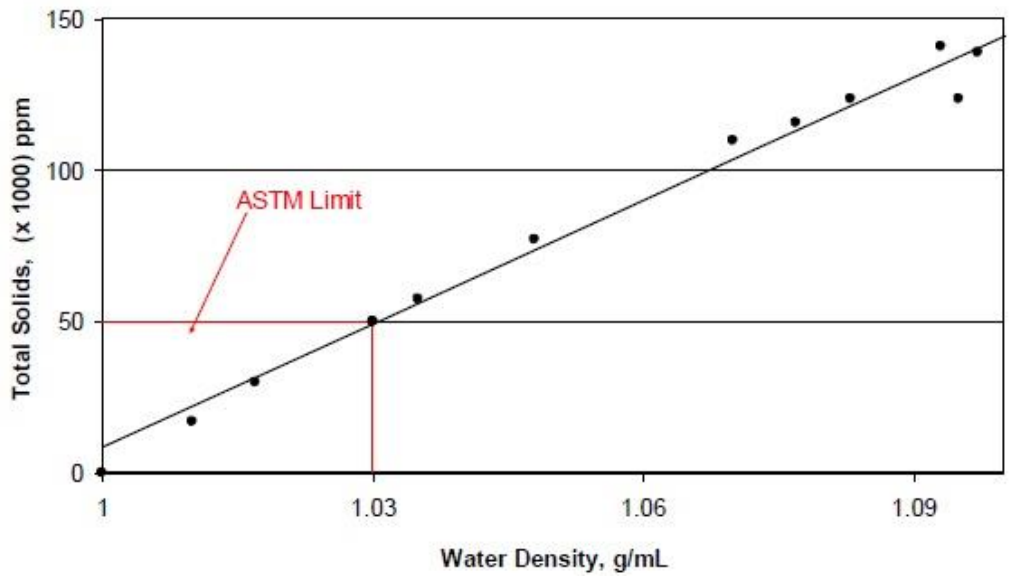

Figure 2.17 Relationship Between TSS Content and Specific Gravity of Wash Water (NRMCA 2013)

2.19 Research on Use of Untreated Wash Water as Mixing Water

The available literature reveals that research on the reuse of wash water for concrete production started in the early 1970s (Tran 2007). Ullman (1973) and Meininger (1973) published research articles in 1973 and both authors disclosed similar conclusions that wash water can be used as mixing water to make fresh concrete without impairing concrete properties.

Ullman (1973) used wash water samples with a total solids content of 4,600 ppm and suspended solids in the range of 50 to 300 ppm. Concrete mixtures with a cement content of 300 kg/m^3 and air-entrainment about 6% were used. Ullman (1973) reported that the reuse of wash water as mixing water did not affect the strength, slump, air content, or mixing water requirement.

Meininger (1973) studied the effects of total solids content of wash water on concrete properties by using tap water, clarified wash water (small amount of total solids content), and agitated wash water slurry (higher amount of total solids content). The author concluded that the use of clarified wash water produced comparable results as tap water in terms of shrinkage, strength, and mixing water requirement. However, Meininger (1973) also found that wash water with a higher amount of solids content may significantly affect the strength and shrinkage.

The concept of sustainability in concrete industry has gained growing attention in recent years and has contributed to more comprehensive research into the use of recycled materials in concrete (Tran 2007). Many researchers have extensively studied several parameters of wash water and its effects on the properties of concrete when used as mixing water (Matos et al. 2020; Asadollahfardi et al. 2015; Vieira et al. 2016; Tsimas and Zervaki 2010; Su et al. 2002; Sandrolini and Franzoni 2001; Chini et al. 2001; Klus et al. 2017; Coppola et al. 2015). Despite the aspects of wash water that they focused on, almost all the researchers have reached a common conclusion that tap water can potentially be replaced by wash water to produce concrete with or without limitations. Results show that the use of untreated wash water affects fresh concrete properties such as workability and setting time but produced comparable compressive strength. The major reason for this trend is the suspended solids in untreated wash water, and the negative effects on fresh concrete properties aggravated by the total solid content (MacDonald et al., 2020).

Matos et al. (2020) conducted an experimental study to evaluate the effects of recycled wash water on the hydration and the fresh and hardened properties of concrete when used as mixing water. Portland cement with 25% fly ash was used for the study and the concrete mixtures were designed to achieve a 28-day compressive strength of 35 MPa with a W/CM ratio of 0.53. Wash water replacement levels of 0, 25, 50, 75, and 100% were considered for this study. Based on the results, the authors noted that the slump was significantly affected in higher wash water replacement levels and 28-day compressive strengths of the concrete mixtures produced with wash water were also lower than the reference concrete mixture but, nevertheless, 7-day compressive strength values were higher. Besides, the authors also established a conclusion that the Portland – fly ash cement hydration was enhanced as a result of the incorporation of wash water.

Chatveera and Lertwattanaruk (2009) studied the effects of total solid content (in wash water) on various concrete properties, such as compressive strength, workability and setting time, and concluded that wash water with a total solid content of less than 6% is more suitable to be used as mixing water and use of wash water in combination with super-plasticiser and/or fly ash improved the durability of concrete. The authors also found that the setting times of concrete made of wash water were drastically decreased with increasing total solid contents.

Asadollahfardi et al. (2015) conducted an experimental and statistical study to investigate the potentials of using wash water in concrete production. Based on the results obtained from the compressive strength tests for hydraulic mortars, the authors concluded that the mortar specimens made with 50% wash water (50% tap water) had higher 3-day, 7-day,

and 28-day compressive strengths. Mortar mixture made with 100% wash water produced lower compressive strength. However, it should be noted that the authors of this study did not use any water-reducing admixture to improve the consistency of the mortar mixtures. Despite the mortar results, Asadollahfardi et al. (2015) pointed out that the usage of wash water did not affect the flexural or compressive strength of concrete.

Sandrolini and Fransoni (2001) study concluded that the use of recycled wash water resulted in the reduction of concrete capillary water absorption and mortar micro-porosity, which can improve the durability of concrete. Also, the concrete specimens produced with recycled wash water yielded a comparable mean 28-day flexural strength.

Tsimas and Zervaki (2010) studied the properties of concrete made with different types of wash water samples (based on TSS) and analysed the effects of chemical admixtures (both retarder and super-plasticiser) on strength and workability. The authors showed that the concrete produced with higher total solid content was greatly benefitted by the incorporation of the chemical admixtures.

Klus et al. (2017) performed a study to evaluate the performance of wash water in the production of cement composites. Three different types of mortar mixtures with 0, 20, and 50% wash water replacement levels were used for this analysis. The authors concluded that the 7-day and 28-day flexural strengths of the mortar specimens produced with wash water were higher than the reference mortar produced with tap water.

2.20 Research on Use of CO_2-Treated Wash Water as Mixing Water

The concept of carbonation of wash water is relatively new and only a very limited number of studies are available on this topic. Xuan et al. (2016) and MacDonald et al. (2020) have conducted experimental studies to assess the potentials of treating wash water with carbon dioxide (CO_2) to diminish or to eliminate the flaws associated with the untreated wash water when used as mixing water. CO_2 easily carbonates the calcium compounds in cement and hydrating cement (Berger et al. 1972; Goodbrake et al. 1979). Huntzinger et al. (2009) studied the CO_2 sequestration for cement kiln dust and expressed that mineral carbonation for alkaline wastes with rich calcium and silicate phases would be an appealing way to utilise industrial CO_2 emissions. Steinour (1959) proposed a formula (Equation 2.15) to calculate the maximum theoretical CO_2 sequestration extent for cementitious materials.

$$\%Th\ (CO_2)_{max} = 0.785(CaO - 0.7SO_3) + 1.091MgO + 1.420Na_2O + 0.935K_2O$$

Equation 2.15

Based on the equation, the calculated maximum theoretical CO_2 sequestration extent for Brookfield type GU cement (used in this study) is approximately 50.0% by weight of cement (bwc).

Xuan et al. (2016) studied the application of CO_2 sequestration to improve the properties of concrete slurry waste (wash water). The authors stated that the fresh wash water can be considered as a cementitious paste and its theoretical CO_2 sequestration extent is in the range of 27.05 to 31.23%. The authors also concluded that the accelerated mineral carbonation leads to rapid initial strength development and decrease in drying shrinkage.

MacDonald et al. (2020) conducted an experimental study to investigate the potentials of improving the properties of wash water with carbon dioxide. Industrially sourced wash water specimens with a specific gravity of 1.20 were used for this study. Wash water specimens were treated with CO_2 and diluted with potable water to achieve a specific gravity of 1.08 prior to use as mixing water for this study. The authors acknowledged that CO_2-treatment eliminated the concerns on setting time and workability associated with the usage of wash water and also concluded that the concrete and mortar specimens produced with CO_2-treated wash water showed comparable 7-day and 28-day compressive strengths. Furthermore, from the results obtained for mortar specimens, MacDonald et al. (2020) proved that the suspended solids in wash water contribute to strength development and can be considered as a cementitious compound. The authors also indicated that the carbonation of wash water mineralised 27% CO_2 by weight of cement, which is consistent with the extent of CO_2 sequestration stated by Xuan et al. (2016).

2.21 Performance Requirements for Specific Performance (Type S) Admixture (ASTM C494)

When introducing a new material or procedure to the production of concrete it is usual to run a suite of tests to ensure that the material or procedure is not injurious to the general properties of concrete. ASTM C494 (2016) provides a framework for evaluating the impact of chemical admixtures on concrete properties. Generally, an admixture that has a specific performance-enhancing capability (termed a ‘Type S’ admixture) that is not related to water-reduction, set-control or air-entrainment has to be tested to demonstrate that it does not produce any adverse effects on the following concrete properties:

- Setting time
- Compressive strength
- Flexural strength
- Drying shrinkage
- Freeze-thaw resistance

To do this, a concrete mixture is produced with the admixture and a control mixture is produced without the admixture (with otherwise identical proportions). The concretes are tested for the properties listed above and the admixture is considered acceptable for use provided that the results of the tests do not deviate by more than a certain amount from the results for the control mixture. For example, the compressive and flexural strength of the concrete with the admixture must be no less than 90% of the strength of the control mixture at all ages. An additional requirement is that the durability factor (DF) of an air-entrained concrete containing the admixture must be at least 80% when tested in cyclic freezing and thawing (ASTM C666 2015).

Chapter 3. Materials and Methods

3.1 Introduction

This chapter illustrates the experimental procedures of this research study in detail. All the experimental works are grouped into three major sections; chemistry of wash water, analysis of mortar, and analysis of concrete. Several chemical properties of wash water, such as pH, chemically bound water (CBW) content, and the concentration of cations and anions were analysed. Several mechanical properties of concrete and mortar, including workability, resistivity, and compressive strength, were also examined. An overview of the experimental work of this study is graphically presented in Figure 3.1.

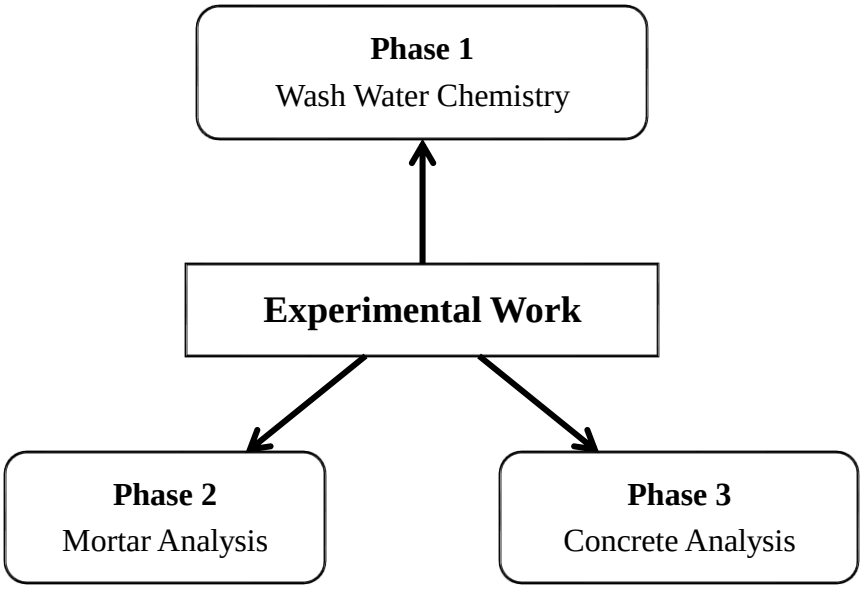

Figure 3.1 Overview of Experimental Work

3.1.1 Preparation of Wash Water

In order to perform any experimental work in this research, the first step was to prepare an adequate amount of wash water sample. Wash water specimens with a specific gravity of 1.10 were used throughout this research study. Table 3.1 shows the parameters for the maximum theoretical carbonation of 1-litre wash water. Based on the requirement, sufficient amount of wash water was prepared by mixing Portland cement and tap water with a cement-to-water ratio of 0.157 (by mass). The prepared wash water sample was allowed to be partially hydrated for 3 hours. Throughout this period, wash water slurry was agitated by constantly stirring it to prevent hardening of the paste. Initial pH and pH reported after 3 hours were measured using a pH meter. The specific gravity of the slurry was also measured at the same time using a hydrometer.

Table 3.1 Parameters for Steinour Maximum (50% bwc) Carbonation of 1-litre Wash Water

Volume (l)	Water (l)	Cement (g)	SG	pH	Required CO_2 (g)	CO_2 (LPM)	Time (min)	New Vol. (l)	New pH
1.00	950.7	149.3	1.10	13.0	74.6	6.6	6.3	1.09	7.0

3.1.2 Treatment for Wash Water

An experimental setup was assembled using a 120-litre plastic container, a submersible pump, and a CO_2 tank (see Figure 3.2). The wash water slurry prepared in section 3.1.1 was transferred to the bin and then treated by injecting CO_2 gas into the slurry through the submersible pump.

Since the carbonation is an exothermic chemical reaction, heat energy is released during the process and it increases the temperature of the slurry. To overcome this issue, a cooling system was incorporated in the experimental setup. The pH of the slurry was monitored during the process and the CO_2 injection was ceased once the pH reached 7.0. Although the maximum theoretical CO_2 sequestration extent is 50% by weight of cement (bwc), in practise, the CO_2 uptake measured after treating wash water with CO_2 in the manner shown in Figure 3.2 has been found to be limited to about 30% (bwc). Beyond this point, unreacted CO_2 bubbles are observed at the surface of the wash water tank. This point typically occurs after approximately 3 hours of CO_2 treatment (when treating 30-litre of wash water) and appears to coincide with the pH of the wash water reaching and maintaining a steady value of 7. The limited uptake of CO_2 could be due to the formation of a calcite layer around the cement particles in wash water which serves to protect the underlying unreacted cement particles. This phenomenon is further elaborated in Chapter 4. The specific point of maximum CO_2 uptake (where pH is 7.0) is designated as 100% CO_2-treatment in this study.

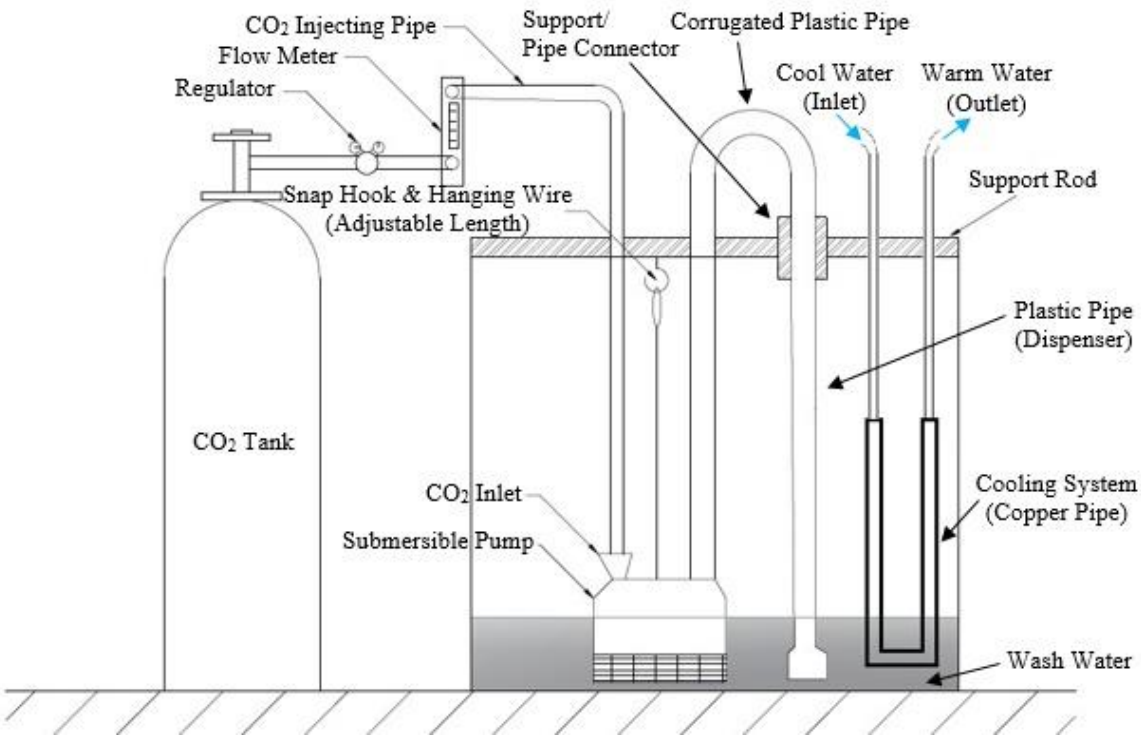

Figure 3.2 Schematic Diagram of Wash Water Treatment Setup

3.2 Chemistry of Wash Water

Several chemical analyses were done on both CO_2-treated and untreated wash water specimens to determine the concentrations of anions and cations present and to investigate the changes in the chemical composition of the specimens over time. The pH of 100% CO_2-treated wash water specimens was also measured over time.

3.2.1 Specimen Storage and Separation of Solid and Liquid Phases

Six representative specimens (200 ml each) were collected separately from both untreated and CO_2-treated wash water slurries for the chemical analyses. Specimens were tested at six different ages; immediately after sampling, and 1, 3, 24, 72, and 168 hours after sampling. The specimens were kept in a roller machine (see Figure 3.3) with a speed of 5

rpm until the testing time to prevent hardening of the cement paste and to avoid segregation of solid and liquid phases. A centrifuge was used to separate solid and liquid phases.

Figure 3.3. Custom-Made Roller Machine

3.2.2 XRD Analysis

The solid phase was dried in a vacuum oven at 40 ºC. Once dried, powder samples were prepared and tested by X-ray diffraction (XRD) to identify crystalline phases. The XRD analysis was conducted at the Department of Earth Sciences, University of New Brunswick. X-ray diffractograms were obtained using a Bruker D8 Advance spectrometer. The source of X-ray was a sealed 2.2 kW Cu X-ray tube that operated at a voltage and current of 40 kV and 25 mA, respectively. Samples were scanned in the range of 5º-80º 2θ at a speed of 0.02º 2θ per second.

3.2.3 Analysis of Anions

Anions in the liquid phase were analysed using ion chromatography (IC). Chloride (Cl^-) and sulphate (SO_4^{2-}) ion concentrations were analysed. Undiluted and diluted (100 or 200 times) samples were used for the analysis.

3.2.4 Analysis of Cations

Diluted samples (100 or 200 times) were analysed using inductively coupled plasma optical emission spectrometer (ICP-OES) to determine the concentration of cations in the liquid phase. The cations analysed were: sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), aluminium (Al^{3+}), and silicate (Si^{4+}).

3.2.5 Bound Water Analysis

The chemically bound water (CBW) and decomposed calcium hydroxide (CH) contents were determined as per the protocol developed by Avet et al. (2016). The analyses were done on untreated, 25%, 50%, 75%, and 100% CO_2-treated wash water specimens. First, the specimens were put into crucibles and kept in the oven at a temperature of 105 ± 2 ºC until the mass change in a day was less than 5% as outlined in ASTM C642 (2013). After that, the specimens were removed from the oven and weighed. Once weighed, the specimens were heated to a temperature of 400 ± 4 ºC for 2 hours in the furnace. The specimens were cooled in a desiccator for a few minutes and then weighed. The CBW contents were determined from the mass loss (Equation 3.1). After weighing, the specimens were again heated to a temperature of 550 ± 5 ºC in the furnace for 2 hours. The final masses were measured after being cooled in the desiccator. The relative CH contents were also estimated from the mass loss that occurred between 400 to 550 ºC (Equation 3.2). The mass loss that occurs between 400 to 550ºC provides an indication of the amount of CH present, but not all of the mass loss in this range is associated with the decomposition of CH as some water will be lost from other hydrates too (e.g. C-S-H).

$$Bound\ water\ (\%) = \frac{m_{105} - m_{400}}{m_{105} - m_c}$$ **Equation 3.1**

Where: m_c – mass of empty crucible, m_{105} – mass of specimen and crucible after oven-dried at 105 ºC, and m_{400} – mass of specimen and crucible after heated to 400 ºC.

$$m_{400-550}\ (\%) = \frac{m_{400} - m_{550}}{m_{400} - m_c}$$ **Equation 3.2**

Where: m_c – mass of empty crucible, m_{400} – mass of specimen and crucible after heated to 400 ºC, and m_{550} – mass of specimen and crucible after heated to 550ºC.

3.3 Analysis of Mortar

The second phase of this research study was to investigate the fresh and hardened properties such as flow and compressive strength of mortars. Fifteen different mortar compositions were tested; the mixture designs for the mortars are described in Table 3.2 and Table 3.3.

Table 3.2. Mortar Mixture Designations

Mix ID	Description
CTRL	Control mixture with regular tap water
WWU	100% tap water replacement with untreated wash water
WWUC	100% tap water replacement with untreated wash water and reduced cement content*
WWT	100% tap water replacement with 100% CO_2-treated wash water
WWTC	100% tap water replacement with 100% CO_2-treated wash water and reduced cement content*
WWT50	50% tap water replacement with 100% CO_2-treated wash water
WWT50C	50% tap water replacement with 100% CO_2-treated wash water and reduced cement content*
WW50T	100% tap water replacement with 50% CO_2-treated wash water

WW50TC	100% tap water replacement with 50% CO_2-treated wash water and reduced cement content*
CTRL-42	Control mixture with regular tap water (W/C = 0.42)
WWT-42	100% tap water replacement with 100% CO_2-treated wash water (W/C = 0.42)
WWTC-42	100% tap water replacement with 100% CO_2-treated wash water and reduced cement content* (W/C = 0.42)
CTRL-55	Control mixture with regular tap water (W/C = 0.55)
WWT-55	100% tap water replacement with 100% CO_2-treated wash water (W/C = 0.55)
WWTC-55	100% tap water replacement with 100% CO_2-treated wash water and reduced cement content* (W/C = 0.55)

*The amount of the cement reduction was equal to the solids content in the wash water

Table 3.3. Mortar Mixture Proportions

Mix ID	Sand:Cement :Water	Cement (g)	C778 Graded Sand (g)	Tap Water (ml)	Untreated WW (ml)	CO_2-Treated WW (ml)
CTRL	2.75:1:0.485#	740.0	2,035.0	359.7	0	0
WWU		740.0	1,987.5	0	377.6	
WWUC		683.6	2,035.0	0	377.6	
WWT		740.0	1,938.1	0	0	396.2
WWTC		655.5	2,009.5	0		396.2
WWT50		740.0	1,988.6	179.5		198.1
WWT50C		697.8	2,024.2	179.5		198.1
WW50T		740.0	1,964.5	0		386.9
WW50TC		669.6	2,023.8	0		386.9
CTRL-42	2.92:1:0.42#	740.0	2,160.8	311.4		0
WWT-42		740.0	2,079.1	0		343.0
WWTC-42		666.8	2,140.9	0		343.0
CTRL-55	2.58:1:0.55#	740.0	1,907.5	407.8		0
WWT-55		740.0	1,800.1	0		449.1
WWTC-55		644.2	1,880.9	0		449.1

#The water-to-cement (W/C) ratios of the mortar mixtures with wash water (untreated or CO_2-treated) were calculated using the water contents of the wash water

3.3.1 Preparation of Mortar Mixtures

Type I (GU) Portland cement with a specific gravity of 3.15 (see Appendix B for complete mill test report) and graded standard sand conforming with ASTM C778 (2017) were used throughout this study to make mortar specimens. All mortar mixtures were prepared as per ASTM C305 (2014). The mortar mixture prepared with 100% tap water was used as a reference mixture (control). For the remaining mortar mixtures, a specific dosage (50-150 ml/ 100 kg of cement) of SP (Euclid™ Plastol 6400) was used to match the workability (as measured by flow) of the control mixture.

3.3.2 Flow of Mortar

The flow of mortar mixtures was determined in accordance with ASTM C1437 (2015). Figure 3.4 shows the measurement of flow of mortar mixtures. Due to the presence of high solid content in wash water, the workability of mortar mixtures produced with wash water was significantly affected. Hence, SP (Euclid™ Plastol 6400) was used to improve the workability of the mortar mixtures. The dosages of SP were established to produce mortar mixtures having a flow of 90-110% that of the control mortar mixture.

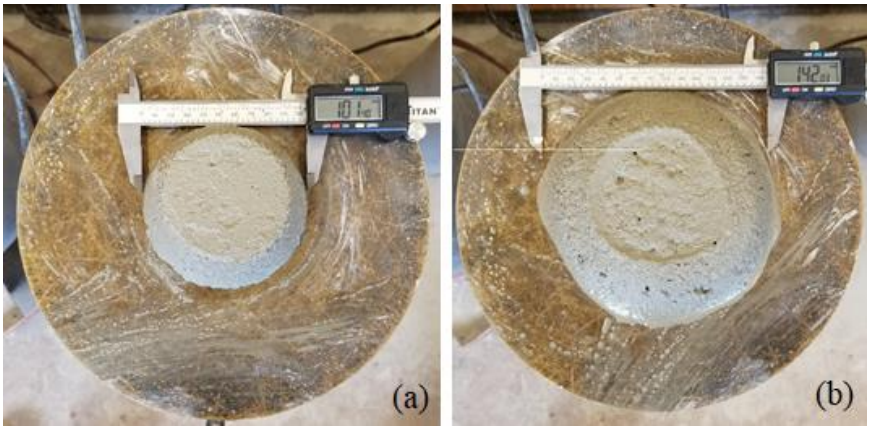

Figure 3.4 Flow of a Mortar Mixture (a) before and (b) after 25 drops of the table

3.3.3 Compressive Strength of Mortar Specimens

Mortar specimens (50 x 50 x 50 mm) were prepared as per ASTM C109 (2016) and cured in saturated lime water at room temperature (23 ± 2 ºC) until the specimens reached the time of testing (except the mortar specimens used for 1-day compressive strength test). The compressive strengths of the mortar specimens were determined using a compressive strength testing apparatus, with a loading rate of 1.2 kN/s, at the ages of 1-day, 7-day, and 28-day as per ASTM C109 (2016).

3.4 Analysis of Concrete

The final phase of this study involved the production of concrete specimens and testing of various fresh and hardened concrete properties. Seven different concrete mixtures were produced and tested; details of the concrete mixtures are presented in Table 3.4 and Table 3.5.

Table 3.4. Concrete Mixture Designations

Mix ID	Description
CTRL	Control mixture with regular tap water
WWU50	50% tap water replacement with untreated wash water
WWU	100% tap water replacement with untreated wash water
WWT50	50% tap water replacement with 100% CO_2-treated wash water
WWT	100% tap water replacement with 100% CO_2-treated wash water
WWTC	100% tap water replacement with 100% CO_2-treated wash water and reduced cement content*
WW50T	100% tap water replacement with 50% CO_2-treated wash water

*The amount of the cement reduction was equal to the solids content in the wash water

Table 3.5. Concrete Mixture Proportions

Mix ID	W/C Ratio	Water Replacement Level (%)	Batch Quantities (kg/m^3)					
			Portland Cement	Tap Water	Untreated WW	CO_2-Treated WW	Coarse Agg.	Fine Agg.
CTRL	0.45[#]	0	400	180	0	0	1,000	691
WWU50		50		90	104	0		678
WWU		100		0	208	0		666
WWT50		50		90	0	111		669
WWT		100		0	0	222		647
WWTC		100	356	0	0	222		684
WW50T		100	400	0	0	215		656

[#]The water-to-cement (W/C) ratio of the concrete mixtures with wash water was calculated using the water contents of the wash water

3.4.1 Fresh Concrete Properties of Concrete Mixtures

Type I (GU) Portland cement with a specific gravity of 3.15 was used to produce concrete mixtures. A cement content of 400 kg/m^3 and a W/C ratio of 0.45 were used for all concrete mixtures. All concrete mixtures were cast in 80-litre batches using a high-shear concrete mixer in accordance with ASTM C192 (2018).

The workability of each concrete mixture was determined using concrete slump test as per ASTM C143 (2015). A target slump range of 125 ± 25 mm was set for all concrete mixtures to produce a workable concrete with a comparable consistency. An adequate dosage of SP (Euclid™ Plastol 6400) was used in each concrete mixture to achieve a slump in the desired range. The air content of each fresh concrete mixture was measured using the pressure method as described in ASTM C231 (2017). The target air content was 6 ± 1% for all concrete mixtures and was achieved by the incorporation of MasterAir® AE200 air-

entraining admixture (AEA). AEA was batched on the fine aggregate since the use of wash water does not affect the dosage of AEA if batched on sand (Ullman 1973). Meininger's (1973) study revealed that the dosage requirement may significantly increase if AEA is batched in wash water.

3.4.2 Casting Concrete Specimens

The following specimens were cast for each mixture as per ASTM C192 (2018),

- Fifteen 100 x 200 mm concrete cylinders
- Three 150 x 300 mm concrete cylinders
- Two 150 x 150 x 530 mm concrete prisms
- Three 75 x 100 x 405 mm concrete prisms

All concrete specimens were kept under wet-burlap immediately after casting to prevent the loss of moisture from the specimens. The concrete specimens were removed from the moulds after 24 ± 2 hours and placed in a moist-curing room for curing at room temperature (23 ± 2 ºC) until the time of testing was reached (except the concrete specimens used for 1-day compressive strength test). The number of concrete specimens used for each test is listed in the table below (Table 3.6).

Table 3.6 Specimens for Various Tests of Concrete

Type of Specimen	Test	Age (days)	No. of Specimens
Cylindrical (100 x 200 mm)	Compressive Strength Test	1	3 (each)
		3	
		7	
		28	
		91	

	Resistivity Tests (Bulk and Surface)	28	3* (each)
		91	
Cylindrical (150 x 300 mm)	Splitting Tensile Test	28	3
Prism (150 x 150 x 450 mm)	Flexural Strength Test (3rd Point)	28	2
Prism (75 x 100 x 405 mm)	Free-Thaw Resistance Test	28	3

*Specimens used for resistivity tests (both bulk and surface) were also used for compressive strength tests as well.

3.4.3 Compressive Strength Test

Concrete specimens were removed from the moist-curing room on the day of testing and both of ends of each concrete cylinder were ground using an end grinder to form smooth cross-sections on both ends. The compressive strength of concrete was determined using three 100 x 200 mm cylindrical concrete specimens in accordance with ASTM C39 (2018).

3.4.4 Bulk Resistivity and Surface Resistivity Tests

The bulk and surface resistivity (28-day and 91-day) of concrete specimens were determined as described in the user manual for RCON™ and AASHTO T358 (2015), respectively. The concrete specimens which were used for the bulk and surface resistivity tests were also used for the compressive strength tests since resistivity tests do not affect any mechanical properties of concrete specimens. Figure 3.5(a) and Figure 3.5(b) show the measurement of the bulk and surface resistivity of a concrete specimens, respectively. The corrected surface resistivity (explained in Section 2.12.1) of concrete specimen was calculated using Equation 3.3.

$$Corrected\ Surface\ Resistivity = \frac{Measured\ Surface\ Resistivity}{1.95}$$ **Equation 3.3**

Figure 3.5 Measurement of (a) Bulk and (b) Surface Resistivity of a Concrete Specimen

3.4.5 Splitting Tensile Strength Tests

The splitting tensile strength of concrete was determined using three 150 x 300 mm cylindrical concrete specimens, at a constant loading rate of 1.0 MPa/min, as per ASTM C496 (2017). The mounting and aligning of specimen on the apparatus was performed with extra caution as the test is prone to errors if the specimen is not properly oriented. The schematic diagram of the splitting tensile testing is shown in Figure 3.6. The following equation was used to calculate the splitting strength (Equation 3.4) (ASTM C496):

$$T = \frac{2P}{\pi l d}$$ **Equation 3.4**

Where: T – splitting tensile strength (MPa), P – maximum applied load indicated by the testing machine (N), l – length of specimen (mm), and d – diameter of specimen (mm).

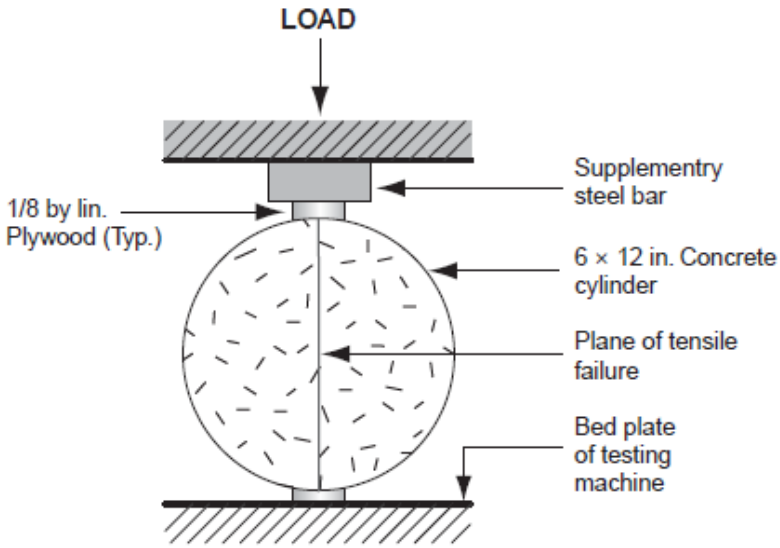

Figure 3.6 Schematic Diagram of the Splitting Tensile Testing (Mehta and Monteiro 2006)

3.4.6 Flexural Strength Tests

Two 150 x 150 x 450 mm concrete prisms were used to determine the modulus of rupture of each concrete mixture. The tests were conducted in accordance with ASTM C78 (2018) and modulus of rupture of the concrete specimens was calculated using Equation 3.5 as all the fractures occurred within the middle third of the span length of the concrete prisms. Figure 3.7 shows the schematic diagram of the flexural strength test (note that L = 450 mm in these tests).

$$R = \frac{PL}{bd^2}$$ **Equation 3.5**

Where: R - modulus of rupture (MPa), P - maximum applied load indicated by the testing machine (N), L - span length (mm), b - average width of specimen (mm), and d - average depth of specimen (mm).

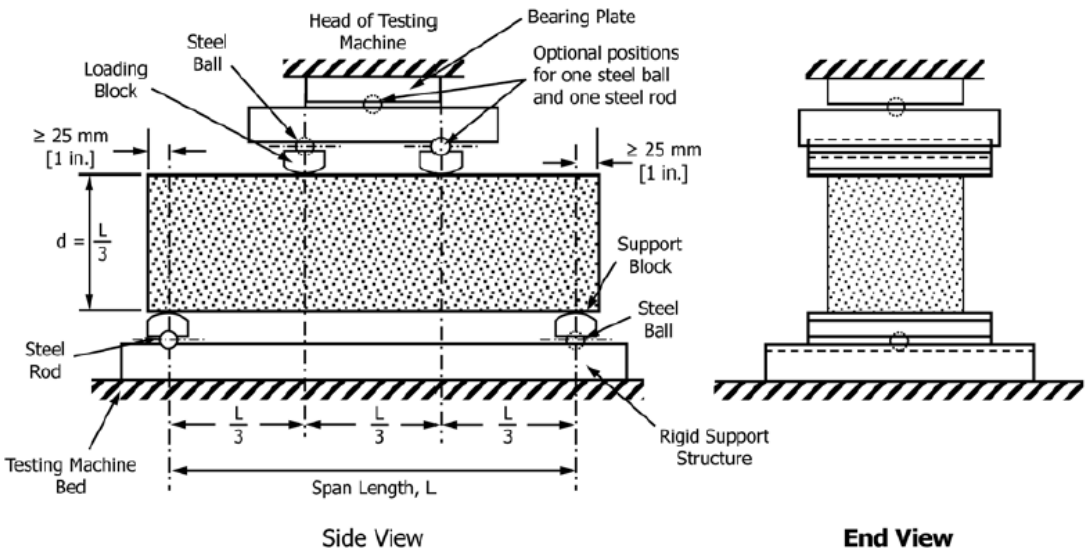

Figure 3.7 Schematic Diagram of the Flexural Strength Testing (ASTM C78 2018)

3.4.7 Freeze-Thaw Resistance Test

Tests to evaluate the resistance of concrete to rapid freezing and thawing were conducted in accordance with ASTM C666 (2015) Procedure A. Three 75 x 100 x 405 mm concrete prisms from each concrete mixture were used for the test. The freezing-and-thawing apparatus was set to make five freezing-and-thawing cycles in a day; that is 4.8 hours for one complete freezing-and-thawing cycle. The temperature was lowered to -18ºC from 4ºC during freezing and raised to 4ºC from -18ºC during thawing. The temperature was monitored using a temperature probe embedded in the centre of a dummy concrete specimen. Procedure A specified in ASTM C666 (specimens were completely surrounded with water at all times) was followed. Figure 3.8 shows the arrangement of concrete specimens in freeze-thaw apparatus for the freeze-thaw resistance test.

Figure 3.8 Specimen Arrangement in Freeze-Thaw Apparatus

Initial mass and fundamental transverse frequency of each specimen were measured prior to starting the freezing-and-thawing as described in ASTM C215 (2014). The specimens were removed in thawed condition after exposing to 35 complete freezing-and-thawing cycles and the mass and fundamental transverse frequency of each concrete specimen were determined. The measurement of mass and fundamental transverse frequency was repeated at intervals of 35 cycles until the specimens complete 300 freezing-and-thawing cycles. The experimental setup for the measurement of fundamental transverse frequency of concrete specimens is shown in Figure 3.9.

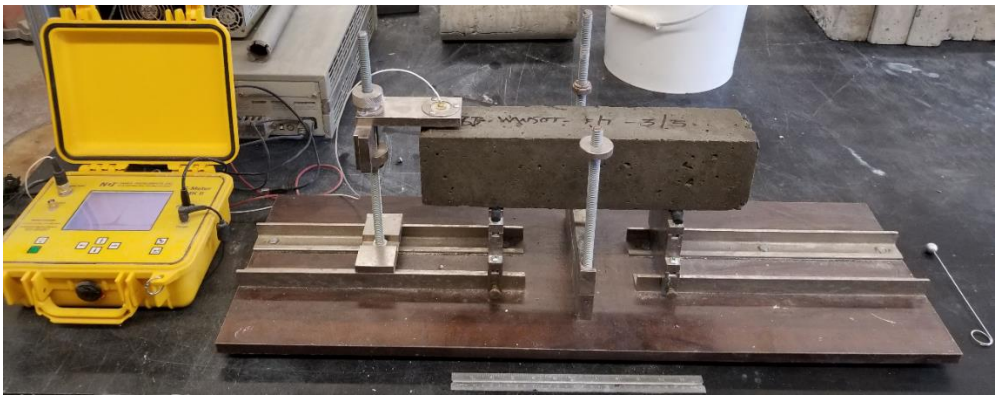

Figure 3.9 Measurement of Fundamental Transverse Frequency of a Concrete Specimen

3.4.7.1 Relative Dynamic Modulus of Elasticity (ASTM C666)

The relative dynamic modulus of elasticity after a specific number of freezing and thawing cycles was measured using the following equation (Equation 3.6) (ASTM C666):

$$P_c = ({n_1}^2/n^2) \times 100$$ **Equation 3.6**

Where, P_c – relative dynamic modulus of elasticity after c cycles of freezing and thawing (%), n – fundamental transverse frequency at 0 cycles of freezing and thawing (in Hz), and n_1 – fundamental transverse frequency after c cycles of freezing and thawing (in Hz).

3.4.7.2 Durability Factor (ASTM C666)

The durability factor (DF) concrete specimen was determined based on the equation below (Equation 3.7) (ASTM C666).

$$DF = PN/M$$ **Equation 3.7**

Where, DF – durability factor of the test specimen (%), P – relative dynamic modulus of elasticity at N cycles (%), N – number of cycles at which P reaches the specified minimum value for discontinuing the test or the specified number of cycles at which the exposure is to be terminated, whichever is less, and M – specified number of cycles at which the exposure is to be terminated. In this study, DF was calculated after 300 cycles.

Chapter 4. Results and Discussion

The overall objective of this study is to investigate the potential of using CO_2-treated wash water with higher TSS content as mixing water to produce concrete. Several laboratory tests were performed to validate the hypotheses made for this study and the results obtained from all the experimental works during the course of this study are presented in this chapter. A detailed discussion is also integrated with each set of results. This chapter is categorised into three major sections as the previous chapter; the first part deals with the results obtained from chemical analyses of several wash water specimens, and the second and third segments are dedicated for the outcomes of numerous mortar and concrete analyses.

4.1 Results of Chemical Analysis

The concentrations of cations and anions in the filtrates of both untreated and CO_2-treated wash water specimens were analysed using ICP-OES and IC. Specific gravity and pH of the specimens were also determined using a hydrometer and a pH meter, respectively. XRD was used to compare changes in phase composition at different ages to assess the effectiveness of CO_2-treatment in preventing further hydration of wash water.

4.1.1 Specific Gravity and pH

The wash water specimens were prepared in-house to achieve a specific gravity of 1.10. The specific gravity of tap water normally assumed as 1.00, but to increase the accuracy of the results, it was measured using a hydrometer capable of measuring specific gravities below 1.00 with an accuracy of ±0.002. The measured specific gravity of tap water was found to be 0.998 and this value was used throughout this study.

The specific gravity and pH of tap water, untreated wash water, and CO_2-treated wash water are tabulated in Table 4.1.

Table 4.1 Specific Gravity and pH of Untreated and CO_2-Treated Wash Water

	TW	WWU	WW25T	WW50T	WW75T	WW100T
SG	0.998	1.100	n.d.	1.115	n.d.	1.130
pH	7.84	13.02	11.51	10.01	8.49	7.01

The level of treatment (carbonation) corresponds to the percentage of CO_2 uptake by the weight of cement present in wash water specimens. 100% CO_2-treated wash water specimens (WWT) refer to, approximately, 30% CO_2 uptake by weight of cement. However, it was determined on the basis of the pH of wash water specimens. Beyond this point, the appearance of CO_2 bubbles from wash water was noticed. This indicated that the cement particles in the wash water were no longer reacting with CO_2. Untreated wash water specimens had a pH of 13.02 and were treated with CO_2 until the specimens had reached the target pH values. 100% CO_2-treatment is achieved when the wash water specimens reach a pH of 7.00. 25, 50, and 75% of the CO_2 treatment levels are at 11.50, 10.00, and 8.50 pH respectively. The specific gravity of 100% CO_2-treated wash water specimens was found to be 1.130.

The pH of 100% CO_2-treated wash water specimens was also measured over time at specified time intervals (0, 1, 3, 24, 72, and 168 hours after CO_2-treatment) and are presented in Table 4.2.

Table 4.2 Change of pH of 100% CO_2-Treated Wash Water Over Time

	WWT0H	WWT1H	WWT3H	WWT1D	WWT3D	WWT7D
Age (hours)	0	1	3	24	72	168
pH	7.01	8.35	9.91	10.26	10.46	10.57

The results show a sharp rise in pH in the first 24 hours after 100% CO_2-treatment and a gradual increase beyond 24 hours. This could be mainly due to the liberation of hydroxyl ions into the aqueous solution.

4.1.2 The Concentration of Cations and Anions

Table 4.3 summarises ion concentrations in tap water, untreated wash water, and CO_2-treated wash water. Filtrates passing through a 0.45 μm filter were used for the analysis. Ion concentrations in tap water were extracted from the 'Water Quality Analytical Results – December 2019' (City of Fredericton, 2020). Chemical limits for mixing water as specified in ASTM C1602 (2018) are also included in the table. The concentrations of aluminium ions in filtrates (diluted 100 or 200 times) were below 0.1 ppm.

Table 4.3 Results of the Concentration of Cations and Anions (ppm)

	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Al^{3+}	Si^{4+}	Alkali [Na_2O Eq.]
TW	33.2	14.0	12.7	0.9	42.4	< 0.1	-	17.9
WWU	32.8	26.5	63.1	739	701	< 3.0	230	671
WWT	29.6	1,610	27.1	667	302	< 3.0	82.8	566
ASTM C1602 Limit	500	3,000	-	-	-	-	-	600

Results show that CO_2-treatment did not affect the concentration of chloride ions in the filtrate, whereas the concentration of sulphate ions was drastically increased after the CO_2-treatment. Despite this radical increase, the sulphate ion concentrations were still below the optional limit of 3,000 ppm according to ASTM C1602 (2018). In addition, chloride ion concentrations before and after carbonation are much lower than the optional limit of 500 ppm outlined in ASTM C1602 (2018) and are comparable to the concentration of chloride ions present in tap water. Gabrisová et al. (1991) reported that ettringite and calcium monosulfoaluminate phases were not stable below a pH of 10.7 and 11.6, respectively, while gypsum and aluminium sulphate phases were stable below these pH levels. This explains the exponential growth in the concentration of sulphate ions due to carbonation as the pH dropped from 13.02 to 7.01.

The concentrations of calcium and silicate ions were also reduced by 57 and 64%, respectively, as a result of the carbonation of wash water. Moreover, alkalis in wash water were also reduced by CO_2-treatment. The concentrations of sodium ions and potassium ions decreased by 57 and 11% respectively. The alkali content (Na_2O Equivalent) of untreated wash water surpassed the optional limit of 600 ppm as specified in ASTM C1602 (2018). However, CO_2-treatment curtailed the alkali content of wash water by 16% which dropped below the optional limit. An assumption was made when calculating the alkali contents (Na_2O Equivalent) that all the sodium and potassium ions present in wash water filtrates were associated with their respective oxides. Thus, the calculated alkali contents are more likely to refer to the maximum equivalent Na_2O concentrations than to the actual alkali content of filtrates (Tran 2007).

Figure 4.1 and Figure 4.2 depict the changes in ion concentrations of CO_2-treated wash water over time. Alkali content (Na_2O Equivalent) was not affected much in the first 3 hours after carbonation. At 1-day, alkali content reached 600 ppm and remained the same until 3 days. The calculated alkali content was 629 ppm after 7 days. The concentration of potassium ions also demonstrated a similar trend. After showing a rapid fluctuation (sudden drop followed by a steep increase) in the first 3 hours, the concentration of sodium ions reached 23 ppm at 1-day and remained the same until 7 days. The calcium ion concentration declined by 20% during the first hour upon carbonation. Afterwards, the concentration of calcium ions increased rapidly up to 24 hours and thereafter exhibited gradual increase. The final calcium ion concentration was 66% higher than its initial concentration. Conversely, the concentration of silicate ions decreased over time. The final concentration of silicate ions was 60% that of initial concentration.

The concentration of chloride ions did not change significantly over the 7 days. Sulphate ion concentration was reduced by 13% within an hour after carbonation, but thereafter the concentration was steadily increased until 7 days. At 7-day, the concentration of sulphate ions reached 1937 ppm, which is 20% higher than the initial concentration of sulphate ions after carbonation.

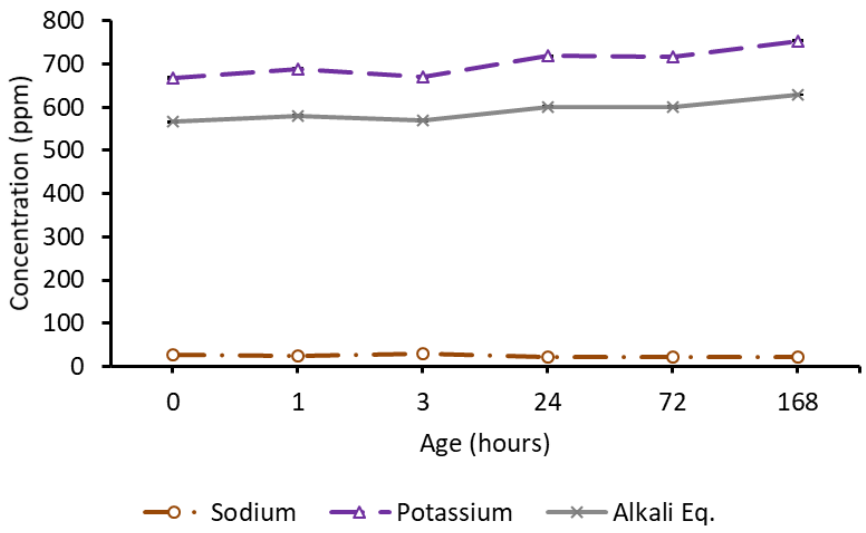

Figure 4.1 Change of Alkalis in 100% CO_2-Treated Wash Water Over Time

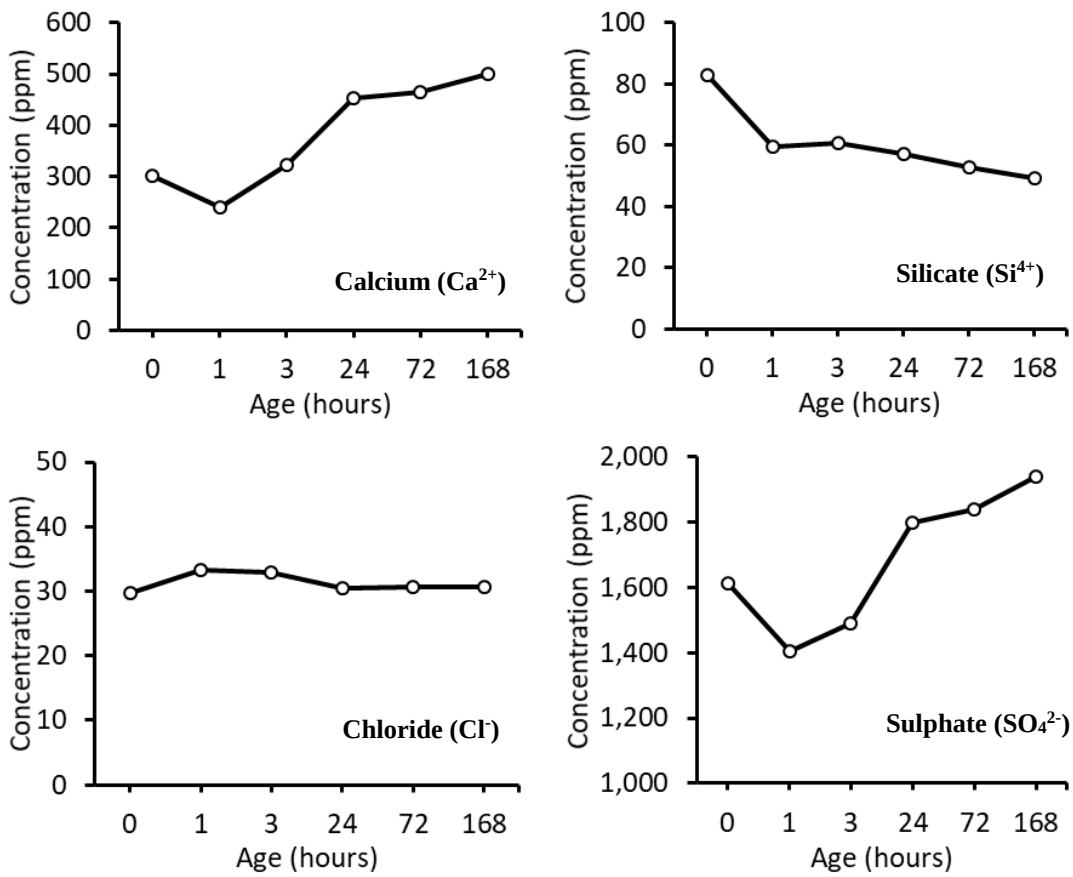

Figure 4.2 Changes in The Concentration of Cations and Anions in 100% CO_2-Treated Wash Water Over Time

4.1.3 CO_2 Sequestration Extent

The carbon contents of solids in untreated and CO_2-treated wash water specimens were determined using a carbon analyser (ELTRA Surface C-800) at CarbonCure Technologies. The test results are presented in Table 4.4. Although the calculated maximum theoretical CO_2 sequestration extent was 50% (bwc), based on the results, 100% CO_2-treatment (WW100T) only mineralised 28.7% CO_2 (bwc). One possible reason for this is the formation of a 'calcite shield' ($CaCO_3$ layer) on the cement particles in the CO_2-treated wash water. This concept is further elaborated in section 4.4.1.1. This calculated value of CO_2 uptake (28.7%) is in agreement with the CO_2 sequestration extents stated by Xuan et al. (2016) and MacDonald et al. (2020).

Table 4.4 Mineralised CO_2 in Untreated, 50% and 100% CO_2-Treated Wash Water

	WWU	WW50T	WW100T
C (%)	0.7	4.6	7.3
CO_2 (%)	2.5	16.9	26.6
% CO_2 (bwc)	2.6	17.7	28.7

4.1.4 XRD Analysis

X-ray diffractograms are useful for tracking any changes that occur in wash water specimens over time. Powdered samples that were dried at 40 ºC in vacuo were used for the XRD analysis. X-ray diffractograms were obtained for untreated and 25, 50, 75, and 100% CO_2-treated wash water specimens at various ages. Figure 4.3 illustrates the effects of carbonation on the mineralogical composition. X-ray diffractograms portray the phase

compositions of the solid phase of wash water specimens before and immediately after various levels of CO_2-treatments. An X-ray diffractogram of Portland cement (type GU) is also incorporated in the plot.

From the plot, it can be seen that the calcium silicate (C_xS) phases were converted to calcium carbonate (C$\underline{C}$) as a result of CO_2-treatment. C$\underline{C}$ peaks are distinctly noticeable at 50% CO_2-treatment level and above. New portlandite (CH) peaks emerged at 18.1º and 51.6º in untreated wash water and 25% CO_2-treated wash water specimens, whereas the magnitude of existing C_xS peaks substantially diminished. It is difficult to distinguish calcium silicate hydrate (C-S-H) peaks as they mostly overlap with other clinker peaks, especially C_xS peaks, and C-S-H has poor crystallography (Kontoleontos et al. 2013). Furthermore, the formation of C-S-H starts after about 2 hours from the beginning of the hydration of cement (Kosmatka et al. 2002). Therefore, C-S-H peaks are unlikely to be observed at an early age.

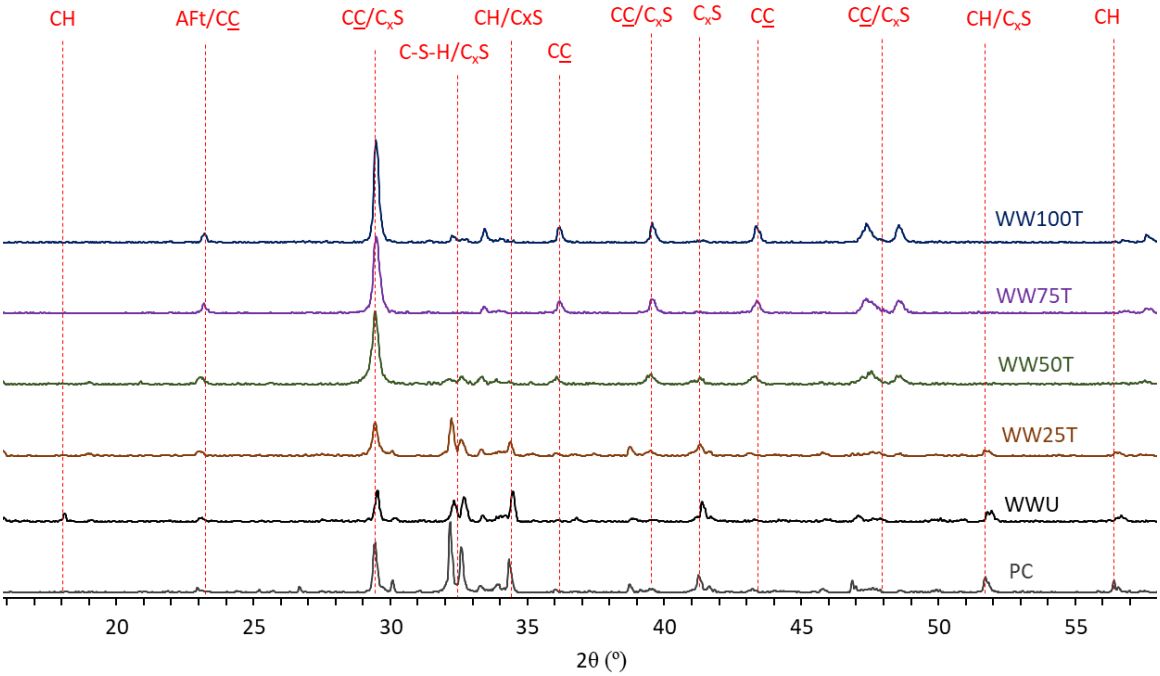

Figure 4.3 X-Ray Diffractograms of PC, Untreated Wash Water, and CO_2-Treated Wash Water Specimens

X-ray diffractograms obtained for untreated to 100% CO_2-treated wash water specimens aged 0, 1, 3, 24, 72, and 168 hours demonstrate the efficacy of CO_2-treatment on prevention of hydration of wash water. Figure 4.4 to Figure 4.8 show the changes in chemical composition that occur at different ages. The enormous growth in CH peak over time can be seen in untreated wash water (Figure 4.4). In addition, ettringite (AFt) and monosulfoaluminate (AFm) peaks increased gradually, while C_xS peaks decreased steadily over time. This clearly indicates the hydration of untreated wash water.

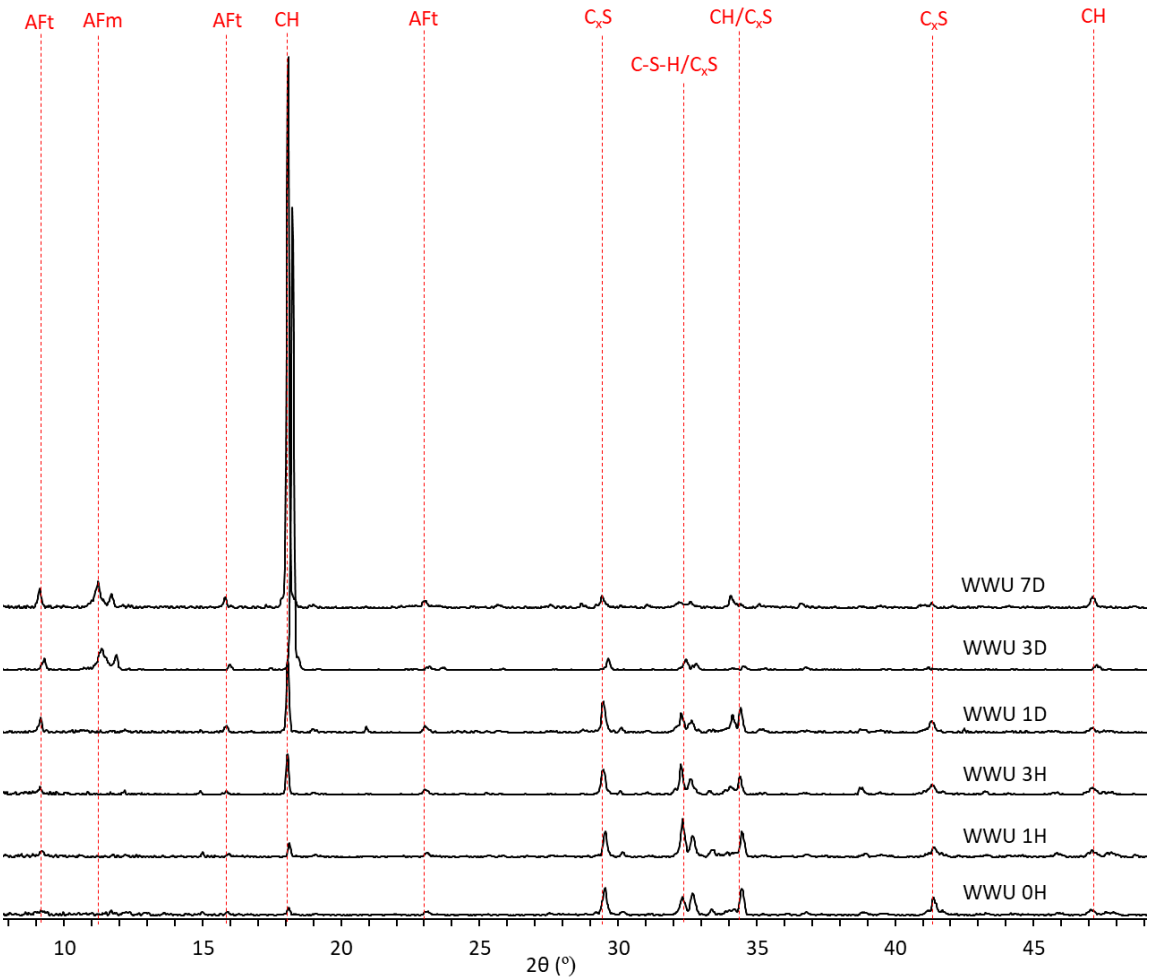

Figure 4.4 X-Ray Diffractograms Obtained for Untreated Wash Water Specimens at Different Ages

The X-ray diffractograms obtained for 25% CO_2-treated wash water (Figure 4.5) also show a similar trend, except the differences in CH and C$\underline{C}$ peaks at 18.1° and 29.4°, respectively. Although 25% CO_2-treated wash water did not produce any sharp peaks of CH at 18.1°, short peaks of CH are noticeable at 18.1° and 47.2°. Besides, as a result of carbonation, C$\underline{C}$ peaks are also present at 29.4°. Notably, AFt peak at 9.1° was curtailed after 3 days whilst AFm peak at 11.3° was further enlarged. This feature is more distinct than that of untreated wash water. Although 25% CO_2-treatment significantly slowed down the hydration of wash water (based on the small CH peaks), the changes in AFt and AFm peaks and a

decrease in the extent of C_xS peaks demonstrate that 25% CO_2-treatment was not successful in completely preventing the hydration of wash water.

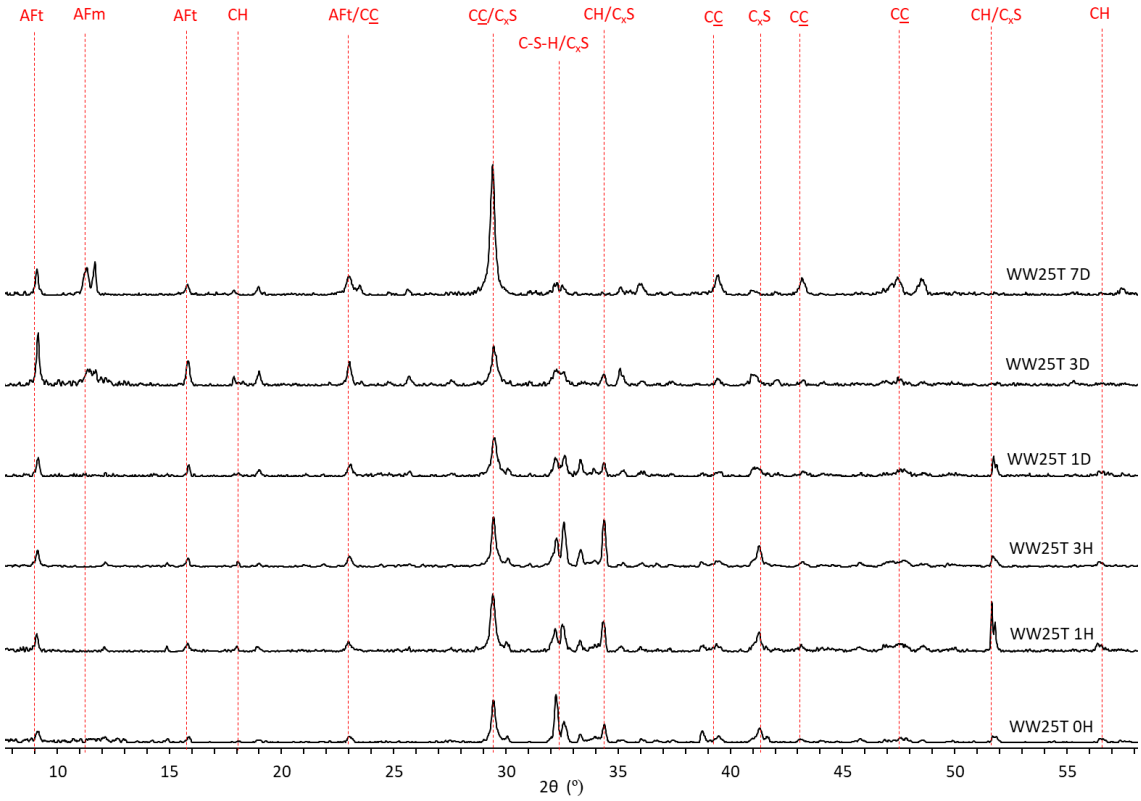

Figure 4.5 X-Ray Diffractograms Obtained for 25% CO_2-Treated Wash Water Specimens at Different Ages

A similar trend was observed in the AFt and AFm peaks in the X-ray diffractograms obtained from 50% CO_2-treated wash water samples (Figure 4.6). A considerable drop in C_xS peaks is also evident in X-ray diffractograms between 3 to 7 days. Considering the magnitude of changes in the AFt, AFm, and C_xS peaks, it can be claimed that 50% CO_2-treatment was effective compared to 25% CO_2-treatment, but not sufficient to completely inhibit the hydration of wash water.

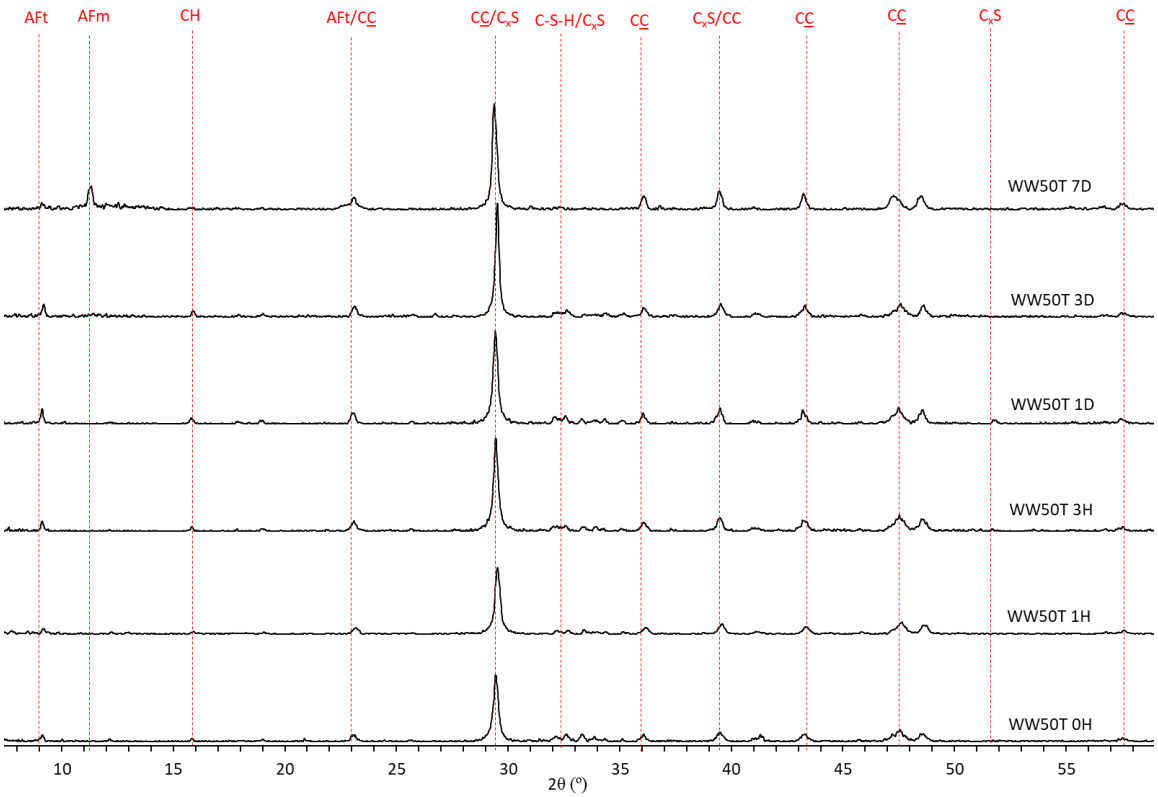

Figure 4.6 X-Ray Diffractograms Obtained for 50% CO_2-Treated Wash Water Specimens at Different Ages

75% CO_2-treatment and 100% CO_2-treatment produced a fairly identical series of X-ray diffractograms (Figure 4.7 and Figure 4.8). Despite the similarities, a significant transition is notable in C_xS/C-S-H peaks at 33.3° in the X-ray diffractograms obtained for 75% CO_2-treated wash water. The C_xS/C-S-H peak was gradually reduced until 3 days, followed by a sudden development of a peak at the same site in 7 days. This suggests that C-S-H was formed as a result of hydration of wash water and that calcium silicates (C_3S and/or C_2S) were exhausted in the process. But such features are absent in the X-ray diffractograms obtained for 100% CO_2-treated wash water samples. This implies that the hydration of wash water in 100% CO_2-treated wash water is implausible. Therefore, based on the overall

results of the XRD analysis, it can be concluded that 75% and 100% CO_2-treatments are effective in arresting the hydration of wash water and 100% CO_2-treatment is relatively more efficient than 75% CO_2-treatment.

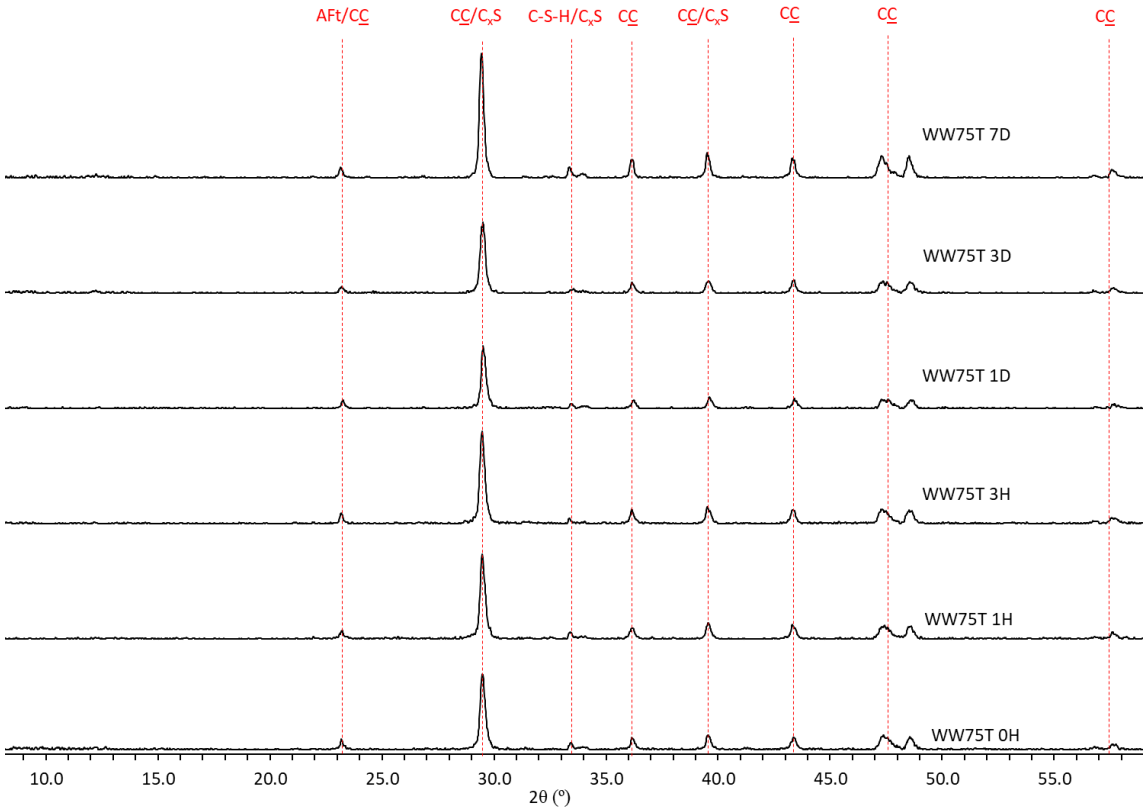

Figure 4.7 X-Ray Diffractograms Obtained for 75% CO_2-Treated Wash Water Specimens at Different Ages

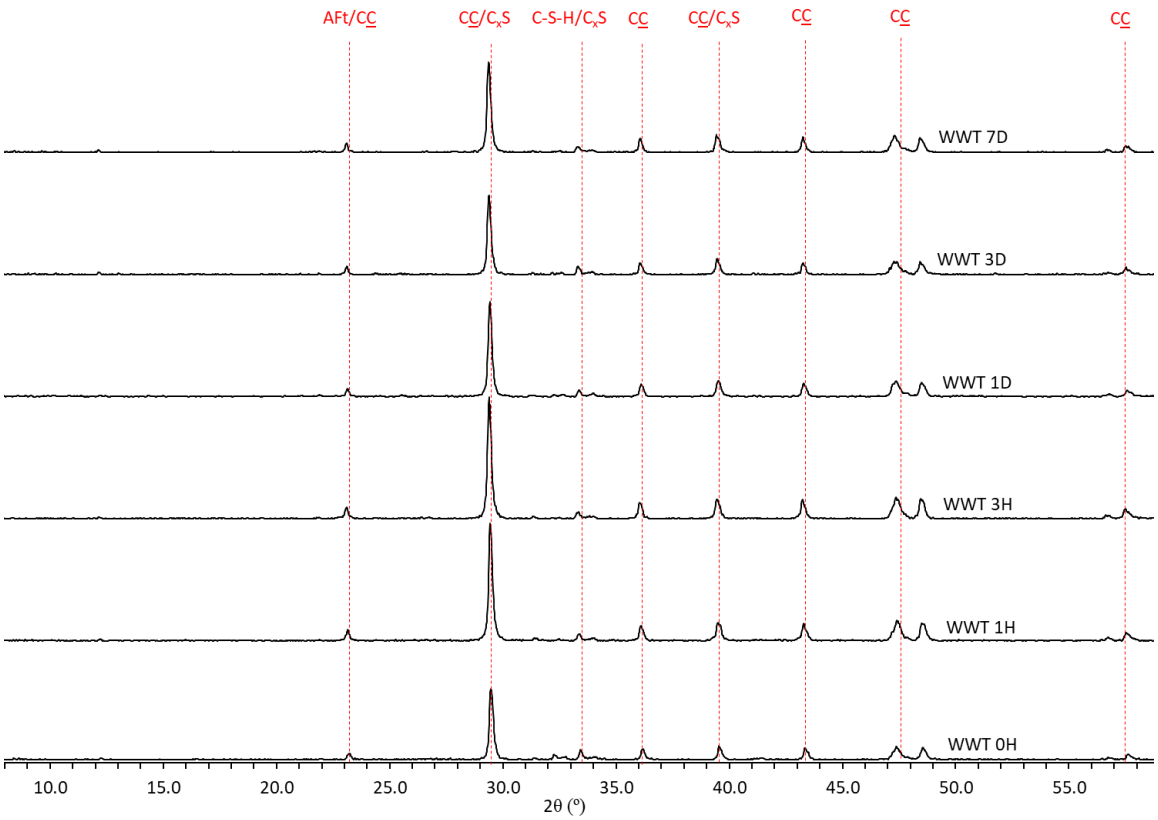

Figure 4.8 X-Ray Diffractograms Obtained for 100% CO_2-Treated Wash Water Specimens at Different Ages

4.1.5 Thermogravimetric Analysis

The thermogravimetric analyses were performed on wash water specimens with different levels of CO_2-treatment at specific ages for the quantification of chemically bound water (CBW) content and the decomposition of CH. The results obtained from TGA are useful to validate the conclusions of the XRD analysis.

4.1.5.1 Chemically Bound Water

The CBW contents of wash water specimens were determined by calculating the mass loss that occurred when the specimens were heated from 105 to 400 ºC. This method is comparatively easy and useful in estimating the hydration of cement paste. Figure 4.9

demonstrates the CBW contents of wash water specimens at different ages. A summary of fresh and 7-day CBW contents for different levels of CO_2-treatment is graphically illustrated in Figure 4.10. 100% CO_2-treated wash water specimen contained a lower CBW content whereas a higher CBW content was exhibited by untreated wash water specimen. Moreover, the rate of increase in CBW content after 7 days is inversely proportional to the level of CO_2-treatment. This suggests that higher levels of CO_2-treatment are more effective in preventing the hydration of wash water.

The increase in CBW with time shown in Figure 4.9 indicates that hydration of cement is occurring. Although the specimens with 25% and 50% CO_2-treatment show increase in CBW, the rate of increase is less than for the untreated specimens. The reduction in rate is likely a combination of the fact that there is less unreacted cement available after these treatments and, possibly, due to the formation of a calcite layer which slows down the hydration of any unreacted cement. For the 75% and 100% CO_2-treated specimens, there is no increase in CBW with time which means that there is no hydration after these treatments. This is possibly because (i) there is very little unreacted cement left that any hydration after treatment is too small to be measurable or (ii) the layer of calcite is thick enough to prevent any hydration of underlying unreacted cement. The latter hypothesis is considered to be more realistic since the CO_2 update was only 28.7% (whereas the maximum theoretical CO_2 extent is around 50%).

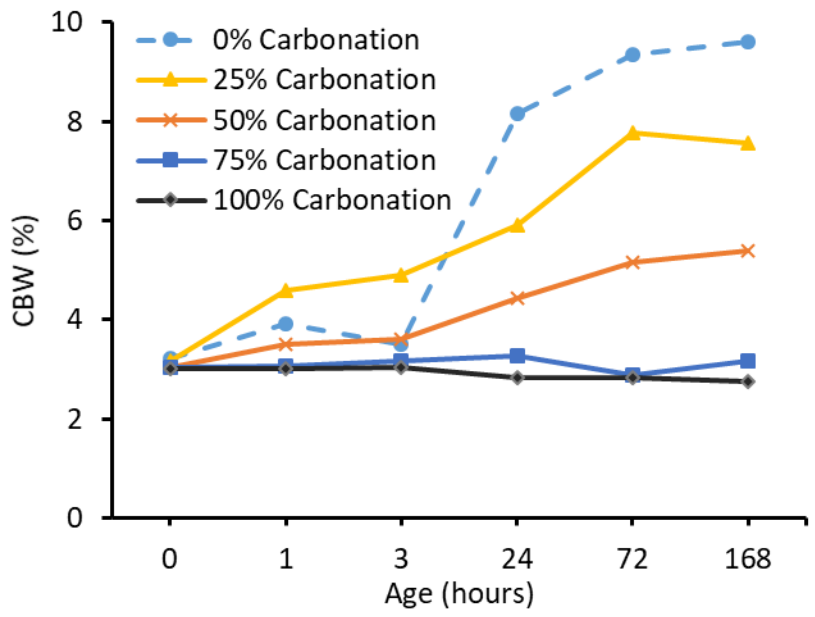

Figure 4.9 CBW Contents of Untreated and CO_2-Treated Wash Water Specimens at Different Ages

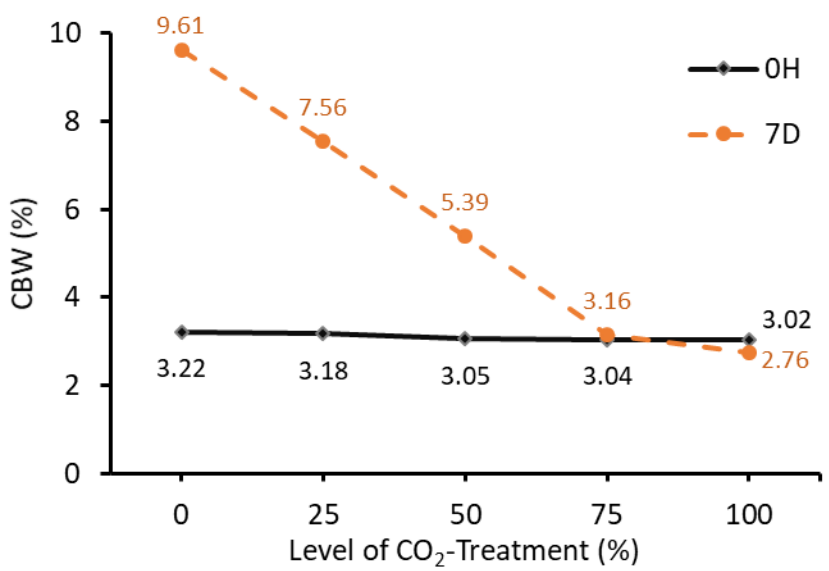

Figure 4.10 CBW Contents of Fresh (0-hour) and 7-day Aged Wash Water Specimens

4.1.6 Decomposition of Calcium Hydroxide

The mass loss occurs when a specimen is heated from 400 to 550 ºC corresponds to the decomposition of CH in the specimen. The change in CH content is also an indicator of the hydration of cement paste specimens. Figure 4.11 shows the changes in CH content of wash water specimens over time. The CH and CBW contents in untreated wash water specimens exhibit a comparable variation. Fresh and 7-day CH contents of wash water specimens are presented in Figure 4.12. A higher content of CH was observed in untreated wash water specimens, while the CH content remained low in 100% CO_2-treated wash water at the initial stage and after 7 days. The CH contents at 0-hour and 7-day follow a similar trend as in the CBW analysis and are inversely proportional to the level of CO_2-treatment. Based on the results, the performances of 75% and 100% CO_2-treated wash water specimens were better than other CO_2-treatment levels in terms of hindering the hydration of wash water since the CH contents remained lower in these wash water specimens throughout the period.

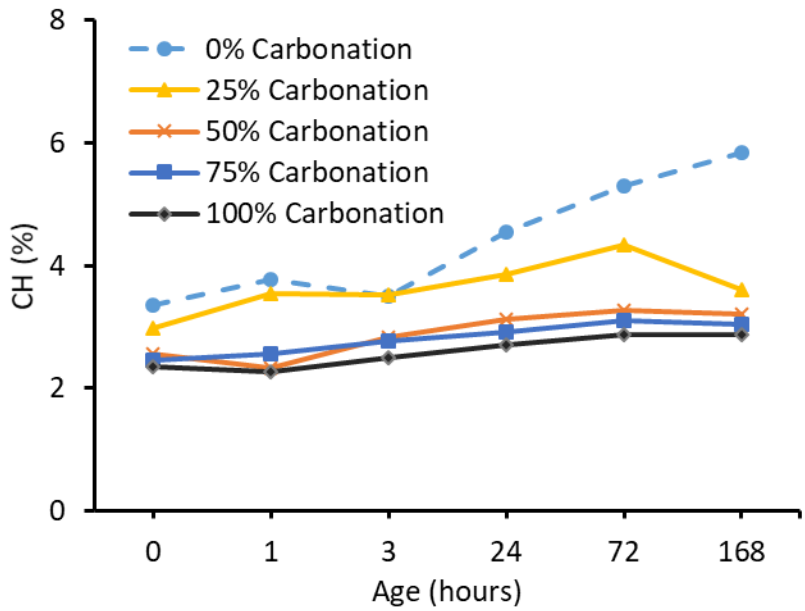

Figure 4.11 CH Contents of Untreated and CO_2-Treated Wash Water Specimens at Different Ages

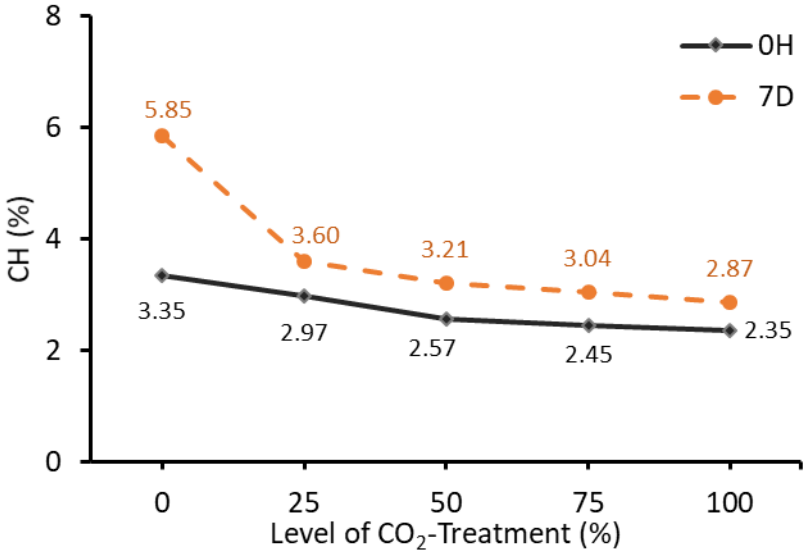

Figure 4.12 CH Contents of Fresh (0-hour) and 7-day Aged Wash Water Specimens

4.2 Results of Mortar Analysis

This section deals with the results of the second phase of this study, i.e. the mortar analysis. Three W/C ratios (i.e. 0.485, 0.42, and 0.55) were used for mortars to assess the effectiveness of CO_2-treatment and to examine the contribution of wash water solids to the strength development. The sand contents were adjusted accordingly in order to maintain a constant volume for all mixtures (mixture proportions are presented in Table 3.3). Mortar mixtures were prepared in accordance with ASTM C305 (2014). In all cases, the strength values reported in this section are the average of three specimens.

4.2.1 The Flow of Mortars (ASTM C1437)

The flow of mortar mixtures was measured as per ASTM C1437 (2015). The control mortar mixture (CTRL) was produced without any admixture (i.e. SP). However, SP (Euclid™ Plastol 6400) had to be used for the other mortar mixtures to achieve workability comparable to that of CTRL (±10% flow). The dosage of SP and the flow of each mortar mixture are summarised in Table 4.5. Mortar mixtures with 50% tap water replaced with 100% CO_2-treated wash water (both WWT50 and WWTC50) required a lower dose of SP than the mortar mixtures with 100% tap water replacement to attain a comparable flow.

Table 4.5 Dosage of SP Used and Flow of Each Mortar Mixture

Mix ID*	SP (ml/ 100 kg cem.)	Flow (%)
CTRL	0	127
WWU	150	133
WWUC	100	138
WWT	150	129
WWTC	100	136

WWT50	75	134
WWT50C	50	139
WW50T	150	128
WW50TC	100	137
CTRL-42	100	122
WWT-42	250	125
WWTC-42	150	130
CTRL-55	0	>160
WWT-55	0	>160
WWTC-55	0	>160

*See Table 3.2 for mortar mixture designations

4.2.2 Compressive Strength of Mortars (ASTM C109)

Mortar specimens, having dimensions of 50 x 50 x 50 mm, were prepared and cured in accordance with ASTM C109 (2016). Compressive strength tests were conducted on mortar specimens at ages of 1, 3 and 28 days. Figure 4.13 provides an overview of the results of the mortar compressive strength tests. The mortar mixture with 100% tap water and a W/C ratio of 0.485 was used as a reference mixture (CTRL). Normalised compressive strengths of mortar mixtures, except for CTRL, based on the results obtained for CTRL are presented in Table 4.6.

Mortar mixture produced with untreated wash water (WWU) showed the highest 1-day compressive strength (7% higher than CTRL). Mixes with 100% and 50% tap water replacement with 100% CO_2-treated wash water (WWT and WWT50, respectively) and 100% tap water replacement with 50% CO_2-treated wash water (WW50T) demonstrated comparable 1-day strength which was in the range of 93 to 97% of CTRL. The mortar mixture that replaced tap water and a portion of cement with 100% CO_2-treated wash water

(WWTC) did not perform well in terms of 1-day compressive strength and had the lowest 1-day strength. The 7-day compressive strength of mortars produced with wash water, both untreated and CO_2-treated, revealed better results than CTRL. Similar to 1-day strength, WWU displayed the highest 7-day strength. However, this trend was changed in the results of 28-day compressive strength. WWT outperformed all other mortar mixtures with a greater 28-day strength, which was 120% of CTRL. Other CO_2-treated wash water mortars also demonstrated better performances than CTRL in 28-day tests.

An interesting fact to note is that the 28-day compressive strength of WWTC was comparable to 28-day compressive strength of CTRL. Moreover, mortar with untreated wash water and cement reduction (WWUC) displayed a comparable or higher 7-day and 28-day strength compared to CTRL. This implies that the solids in wash water have cementitious properties and contribute to strength development. Xuan et al. (2016) and MacDonald et al. (2020) also expressed similar conclusions from their studies.

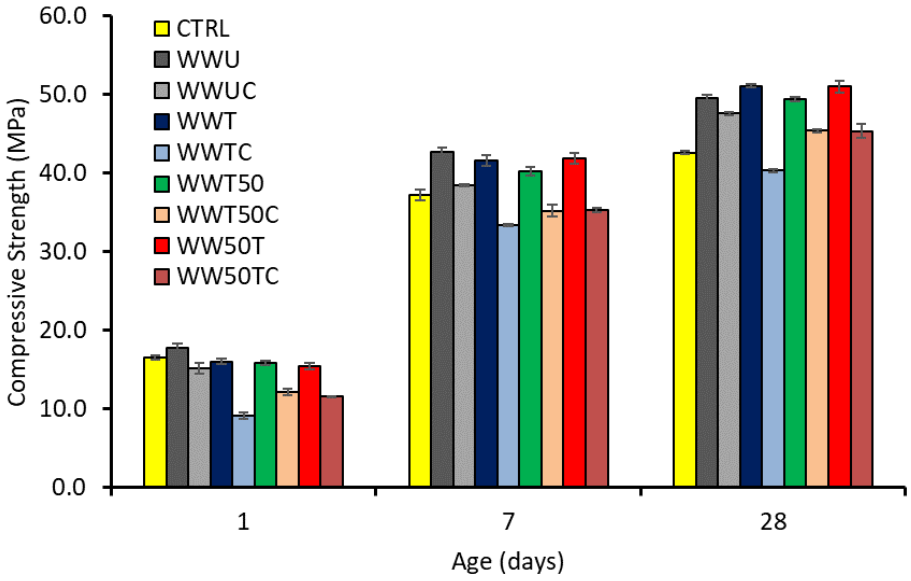

Figure 4.13 Overview of Compressive Strength Test Results of Mortar Specimens (W/C = 0.485)

Table 4.6 Normalised Compressive Strengths of Mortar Specimens (W/C = 0.485)

Compressive Strength	1-day	7-day	28-day
CTRL (MPa)	16.5	37.2	42.6
WWU (%)	106.7	114.2	116.4
WWUC (%)	91.9	103.3	111.6
WWT (%)	97.0	111.6	119.9
WWTC (%)	55.2	89.8	94.6
WWT50 (%)	95.8	108.1	116.0
WWT50C (%)	73.3	94.6	106.6
WW50T (%)	93.3	112.6	119.7
WW50TC (%)	69.7	94.9	106.3

4.2.3 Mortar Mixtures with Different W/C Ratios

In order to investigate the ability of solids in CO_2-treated wash water to influence the strength development, mortar mixtures with a W/C ratio of 0.42 and 0.55 were also considered. Figure 4.14 depicts the test results. WWT achieved the highest 7-day and 28-day compressive strengths at all three W/C ratios. Moreover, in all three cases, the 28-day strengths of WWT were greater than 110% of CTRL. On the contrary, WWTC displayed the lowest 1-day, 7-day and, 28-day compressive strengths. Still, the 7-day and 28-day strengths of WWTC are comparable to CTRL. Notably, both WWT and WWTC demonstrated a better strength gaining at later ages than CTRL at all three W/C ratios. The gradients of compressive strength vs age plots (Figure 4.14) exhibit this pattern. As such, it can clearly be seen that the solids in CO_2-treated wash water are contributing to the strength development, especially at later ages. Another interesting fact to note is that WWT showed the highest 1-day strength at the W/C ratio of 0.55. Particularly, at higher W/C ratios WWT tends to achieve better strengths at the early ages.

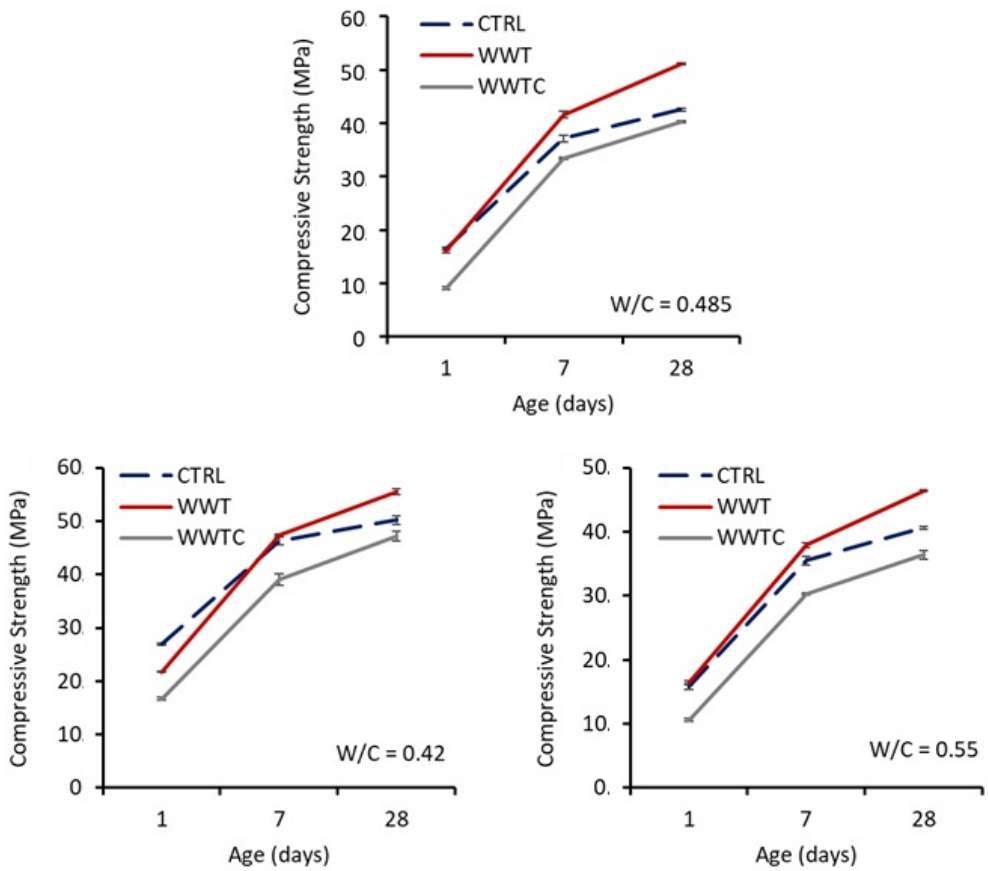

Figure 4.14 Compressive Strength of Mortar Specimens of Different W/C Ratios

Since solids in CO_2-treated wash water revealed cementitious properties, it is sensible to reiterate the results (i.e. the strength of mortars) in terms of water-to-binder (W/B) ratio incorporating the solids provided by CO_2-treated wash water in the denominator (e.g. as 'binder'). Figure 4.15 graphically illustrates the 28-day compressive strengths of CTRL, WWT, and WWTC as a function of W/B ratio and W/C ratio. In fact, WWT shows greater performance even when W/B is considered instead of W/C. This signifies that solids from CO_2-treated wash water contributed to strength development and can be considered as a cementitious material.

Based on the original results (Figure 4.14), it was noted that WWTC demonstrated the least strength among all the mixtures. But the W/C ratio considered for WWTC was not the actual W/C ratio of WWTC. The actual W/C ratio [$(W/C)_t$] was used in Figure 4.15. Based on the graph, the performance of WWTC is not only satisfactory but also better than CTRL at lower W/C ratios. Conversely, the CTRL outperformed WWTC at higher W/C ratios and also when W/B ratio is considered instead of W/C. Considering the facts, replacing cement by the amount of solids provided from CO_2-treated wash water may not be ideal. A partial replacement of Portland cement is possible, but it should be less than the quantity of solids provided by CO_2-treated wash water. The efficiency factor of the solids in CO_2-treated wash water is discussed in the following section, 4.2.4.

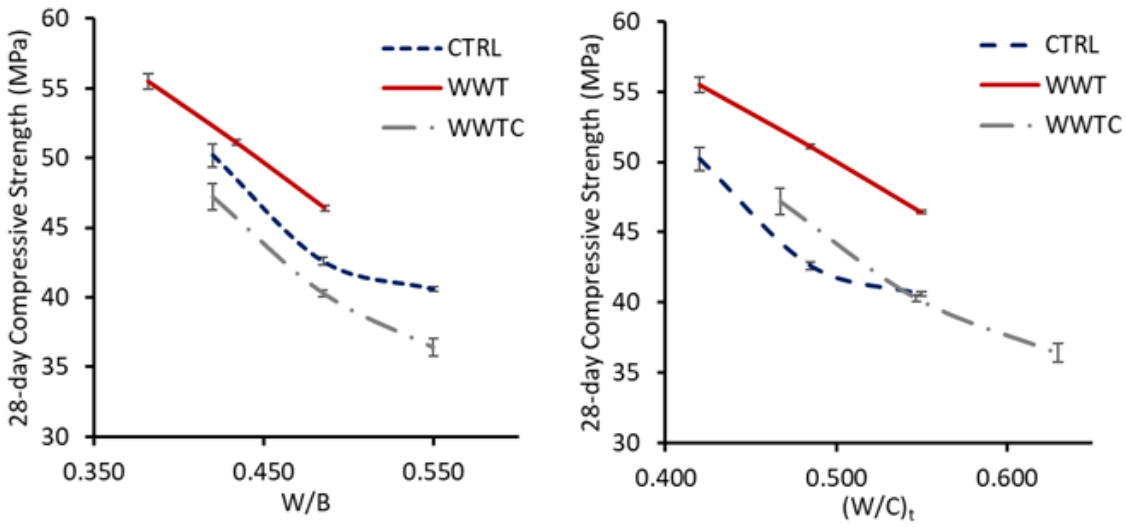

Figure 4.15 28-day Compressive Strength of Mortar Specimens as a Function of W/B and $(W/C)_t$ Ratios

4.2.4 Cementitious Property of Solids in CO_2-Treated Wash Water

The compressive strength results obtained for mortar mixtures with CO_2-treated wash water demonstrated the cementitious properties of the solids in the CO_2-treated wash water specimens. The efficacy of the solids in CO_2-treated wash water in contributing to the strength gain in mortar mixtures was evaluated using the following formula (Equation 4.1).

$$(W/C)_{eq} = \frac{w}{(c + k.s)}$$ **Equation 4.1**

Where, $(W/C)_{eq}$ – equivalent water-to-cement (W/C) ratio, w – mass of water, c – mass of cement, k – efficiency factor, and s – mass of solids in the CO_2-treated wash water.

The efficiency factor of the solids in CO_2-treated wash water was determined on the basis of 7-day and 28-day compressive strength results obtained for mortar mixtures. Least-squares regression method was used for the purpose (Chapra and Canale 2015). The results of this analysis are shown in Figure 4.16. Based on the regression analysis, the efficiency factor of the solids in 100% CO_2-treated wash water was found to be 0.2 and 0.7 at 7-day (k_7) and 28-day (k_{28}), respectively. The calculated efficiency factors (i.e. k_7 and k_{28}) not only validate the cementitious property of the solids in CO_2-treated wash water but also exhibit that the solids in CO_2-treated wash water tend to promote a higher strength development at later ages.

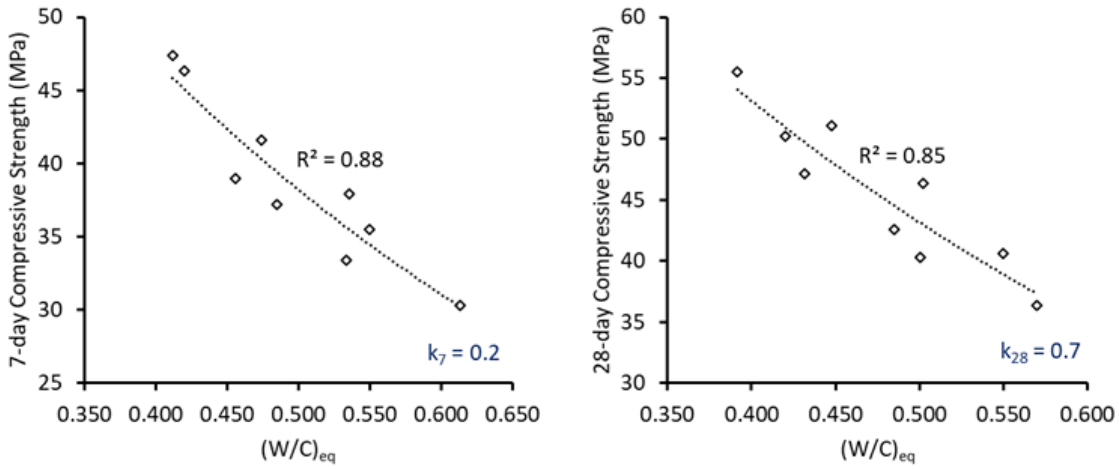

Figure 4.16 The Efficiency Factors of the Solids in 100% CO_2-Treated Wash Water at 7 and 28 day

4.3 Results of Concrete Analysis

The results from all the concrete tests are presented in this section. A W/C ratio of 0.45 was used for all the concrete mixtures. Similar to the mixture design followed for mortar mixtures, the fine aggregate (sand) content of each concrete mixture was adjusted for the purpose of maintaining the same volume across all concrete mixtures. An overview of the mixture proportions is provided in Table 3.5. The results provided in this section are the average of three measurements (or specimens) unless otherwise specified.

4.3.1 Fresh Concrete Properties

Fresh concrete properties such as workability and air content were measured using the slump cone and pressure method, respectively. The dosage of AEA (MasterAir® AE 200) was established on the basis of trial mixtures performed to achieve an air content of 6% for all concrete mixtures and it was found to be 32 ml/ 100 kg of cement. In contrast to AEA, the SP (Euclid™ Plastol 6400) dosage varied across all concrete mixtures and was

determined by visual examination of the mixed concrete. The target was to accomplish a workable slump in the range of 100-150 mm. Initially, a dosage of 300 ml/ 100 kg of cement was added with water (or wash water) and additional SP was added to the mixture when required. Slump and air content of each concrete mixture were measured as per ASTM C143 (2015) and ASTM C231 (2017), respectively. Table 4.7 presents a summary of the results of the slump and air content tests. The results of the slump and air content tests are shown in Figure 4.17 and Figure 4.18, respectively.

The air contents of all concrete mixtures ranged from 5.1 to 5.7% and is considered to be fairly consistent and within the variability of the test method. A similar trend was noticed in the results of workability as well. However, the workability of each concrete mixture was significantly manipulated with different dosages of SP. WWTC gained much higher slump than CTRL (> 140%) with the same dosage of SP. Lower cement content (11% reduction in cement) may have had an impact on the slump. Higher SP dosages were used for other concrete mixtures with wash water to achieve an acceptable slump (100-150 mm). A higher dosage of SP (500 ml/ 100 kg of cement) was used for WW50T to bring the slump above 100 mm.

Table 4.7 Dosages of AEA and SP for Concrete Mixtures

	CTRL	WWU50	WWU	WWT50	WWT	WWTC	WW50T
Air Content (%)	5.6	5.5	5.3	5.3	5.2	5.7	5.1
Slump (mm)	115	105	130	150	120	165	110
AE (ml/ 100 kg cem.)	32	32	32	32	32	32	32
SP (ml/ 100 kg cem.)	300	350	500	400	450	300	500

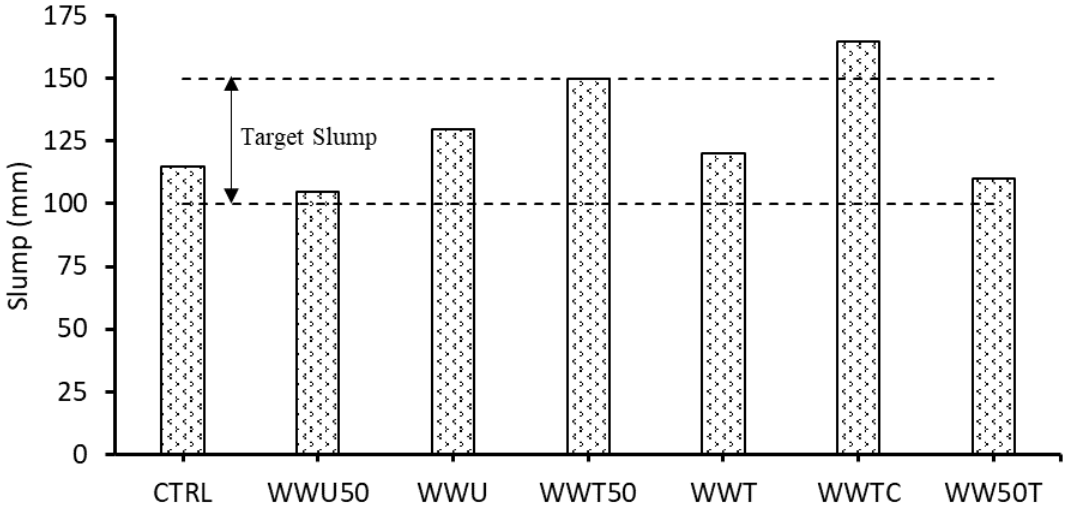

Figure 4.17 Slump of Concrete Mixtures

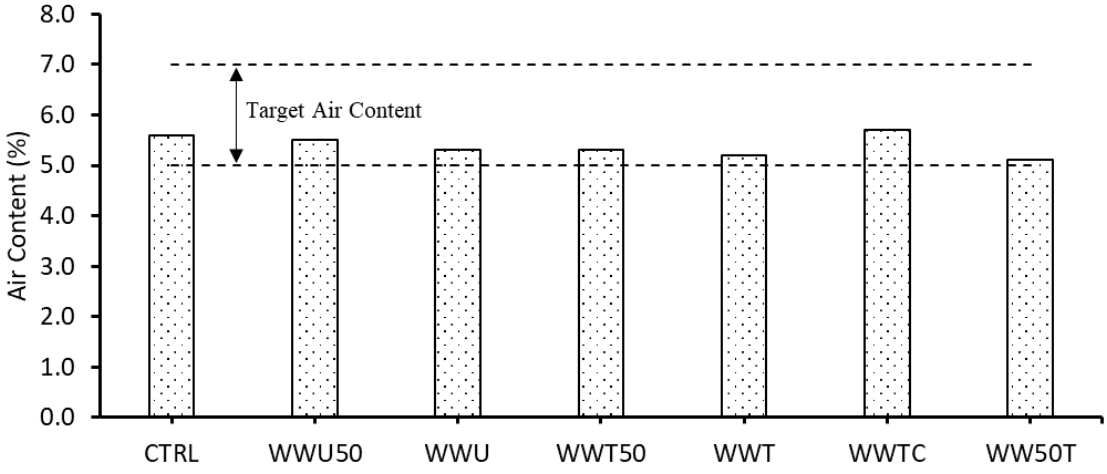

Figure 4.18 Air Contents of Concrete Mixtures

4.3.2 Compressive Strength of Concrete

Cylindrical concrete specimens (100 mm diameter x 200 mm length) were prepared and tested for compressive strength at different ages (1, 3, 7, 28, and 91 days) in accordance with ASTM C192 (2018) and ASTM C39 (2018), respectively. The summary of the test results is depicted in Figure 4.19 and Figure 4.20. Concrete with untreated wash water

(WWU) displayed the highest 1-day and 3-day compressive strengths. Concrete produced with a 50% tap water replacement with 100% CO_2-treated wash water (WWT50) showed a maximum 7-day compressive strength. The highest 28-day compressive strength was observed in concrete with 50% CO_2-treated wash water (WW50T). Based on the results, WWT (concrete with 100% CO_2-treated wash water) demonstrated the highest 91-day strength (~107% that of CTRL). Kosmatka et al. (2002) stated that the use of (high doses) SP tends to substantially increase early strengths and this could possibly be the case for the high early strengths observed in both WWU and WW50T.

WWTC displayed the lowest compressive strengths at all test ages. However, the compressive strengths were in the range of 84-93% that of CTRL, except for the 1-day strength. Although the designed W/C ratio was 0.45, with the cement reduction, the effective W/C ratio was 0.51 for WWTC. The 1-day compressive strength was just 69% compared to CTRL, but it reached 92% of CTRL at 28-day test. This suggests that WWTC is gradually attaining more strength with time compared to CTRL. The performance of WWTC is therefore creditable. Furthermore, all wash water concretes, including untreated and CO_2-treated, satisfy the requirement specified in ASTM C1602 (2018) as the 7-day compressive strengths of these concrete mixtures are above 90% of CTRL.

Another interesting fact to note is that the strength gaining demonstrated by WWT. The 1-day compressive of WWT was 98% that of CTRL, but the greatest strength, 107% compared to CTRL, was achieved by WWT after 91 days. Similar to WWTC, this evidence indicates that 100% CO_2-treatment is promoting strength gaining at later ages. This phenomenon is also pointed out by MacDonald et al. (2020). All the evidences support that

CO_2-treated wash water contributes to strength development and can be considered as a cementitious material.

Type 1 fracture pattern was observed in the majority of 28-day and 91-day test specimens. A fracture pattern of either type 2 or 3 was noticed in the remaining specimens. Figure 4.21 shows a type 1 fracture pattern observed for a concrete specimen. None of the specimens tested for 28-day and 91-day compressive strength showed any other type of fracture pattern.

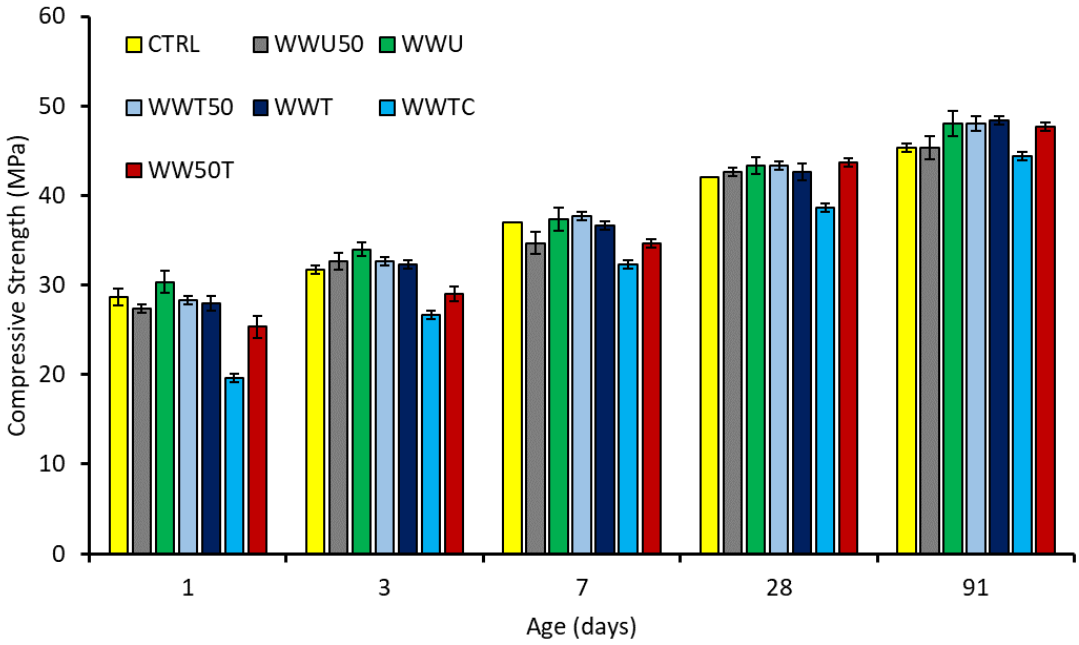

Figure 4.19 Overview of Compressive Strength Test Results of Concrete Specimens

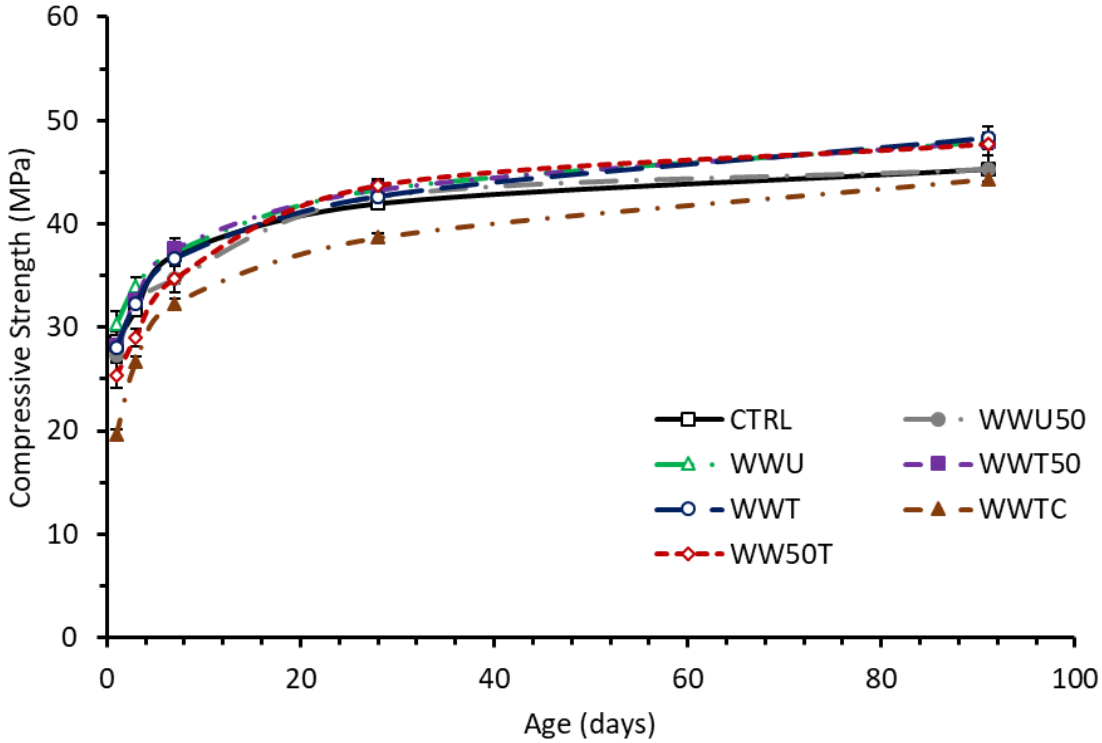

Figure 4.20 Compressive Strength of Concrete Test Specimens vs Age

Figure 4.21 Type 1 Fracture Pattern of a Concrete Specimen

4.3.3 Resistivity of Concrete

Surface and bulk resistivity test results are presented in the following subsections. The concrete specimens prepared for 28-day and 91-day compressive strength tests were also used for both surface and bulk resistivity tests as the resistivity tests are non-destructive and do not alter concrete properties.

4.3.3.1 Surface Resistivity Results (AASHTO T358)

Surface resistivity tests were conducted as per AASHTO T358 (2015). 28-day and 91-day surface resistivity test results are graphically illustrated in Figure 4.22 and Figure 4.23, respectively. Results show that WWU exhibited a higher surface resistivity at both ages. In both cases, the surface resistivity of WWU was more than 110% that of CTRL. The performance of all concrete mixtures, in terms of surface resistivity, was comparable, and even WWTC recorded a 28-day surface resistivity value which was 97% that of CTRL. The surface resistivity of concrete mixtures produced with wash water (untreated or CO_2-treated) were between 97% and 114% of the control mixture.

According to AASHTO T358 (2015), chloride ion penetration is higher in concrete with a surface resistivity value less than 12 kΩ.cm at 28-day (equal to a surface resistivity value of 6.15 kΩ when corrected). All of the concrete specimens tested, except WWU and WWT50, fall into this category.

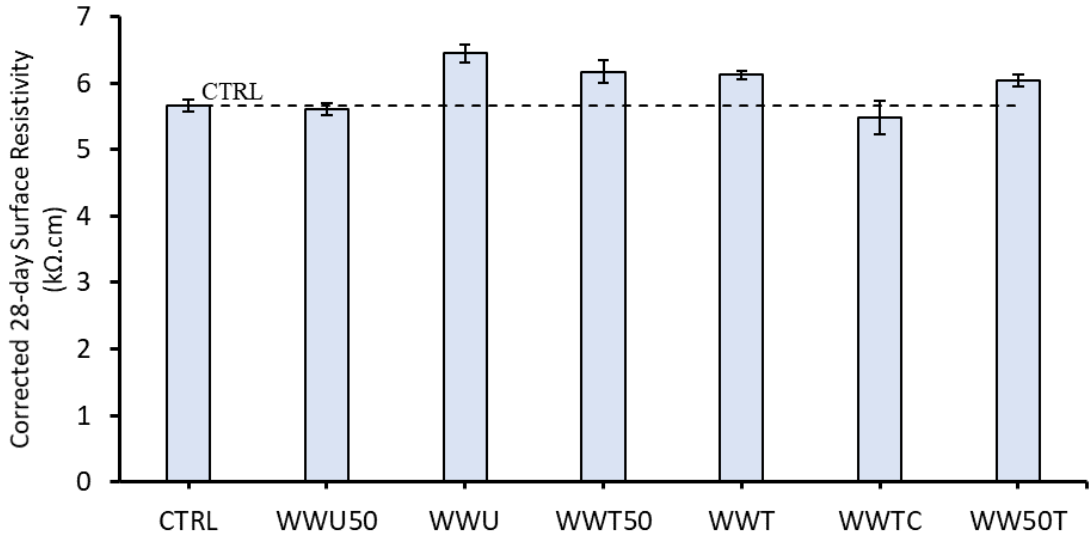

Figure 4.22 28-day Surface Resistivity Test Results of Concrete Specimens

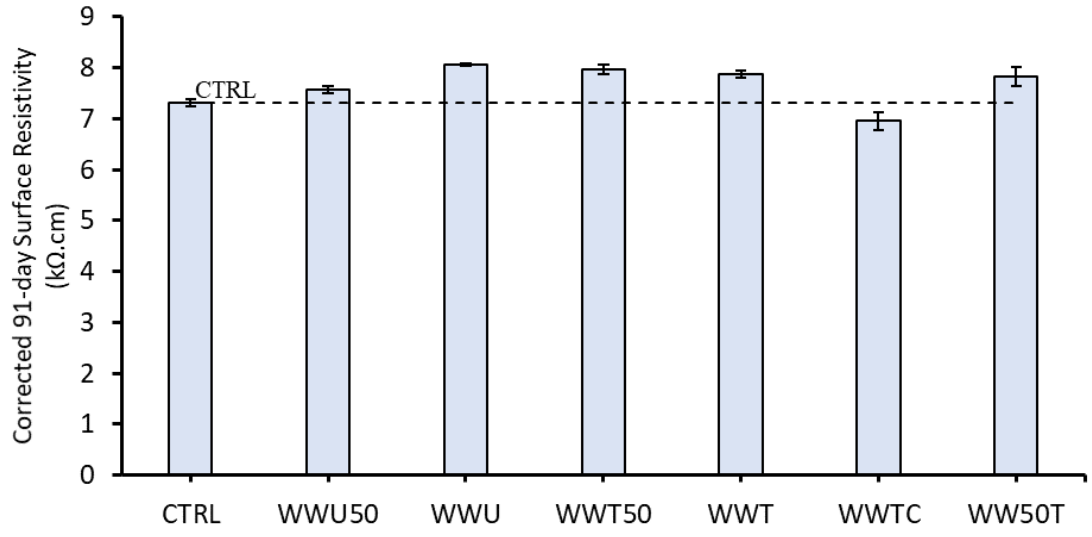

Figure 4.23 91-day Surface Resistivity Test Results of Concrete Specimens

4.3.3.2 Bulk Resistivity Results

Bulk resistivity tests were conducted as per the guideline provided by the manufacturer (Giatec Scientific Inc.). Samples were moist cured until the test age and tested in SSD condition. Figure 4.24 and Figure 4.25 summarise the bulk resistivity test results. WWTC showed the lowest 28-day bulk resistivity among all the concrete mixtures. On the contrary to the surface resistivity test results, WWT demonstrated the highest 28-day bulk resistivity and was 10% greater than CTRL. Nevertheless, WWU attained the highest 91-day bulk resistivity. Notably, all the tested concrete specimens achieved comparable bulk resistivity values in the range of 95-110% that of CTRL.

As specified in the manufacturer's guideline, the bulk resistivity values between 5 and 12 kΩ.cm indicate moderate chloride penetration. Hence, the chloride penetration potential for all of the concrete mixtures in this study is moderate.

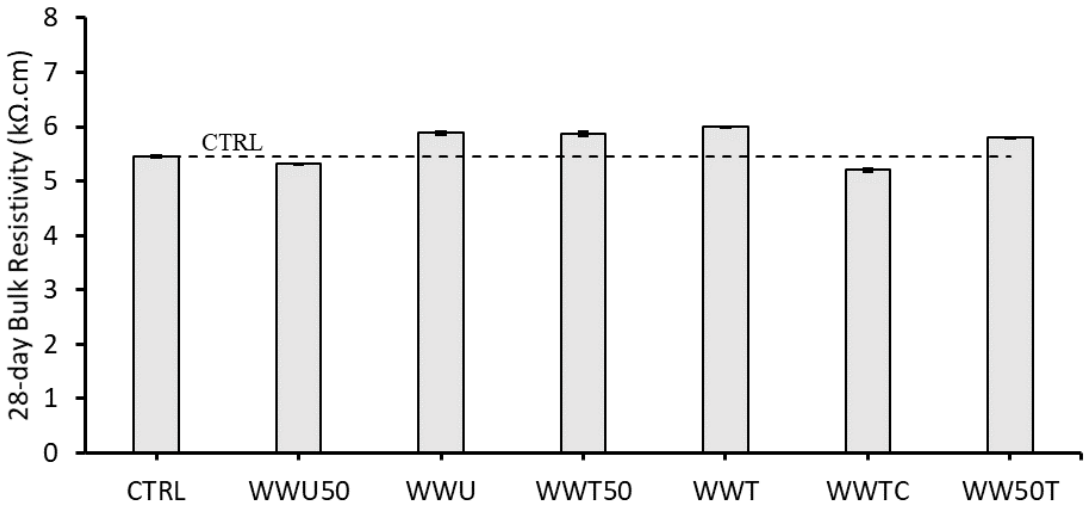

Figure 4.24 28-day Bulk Resistivity Test Results of Concrete Specimens

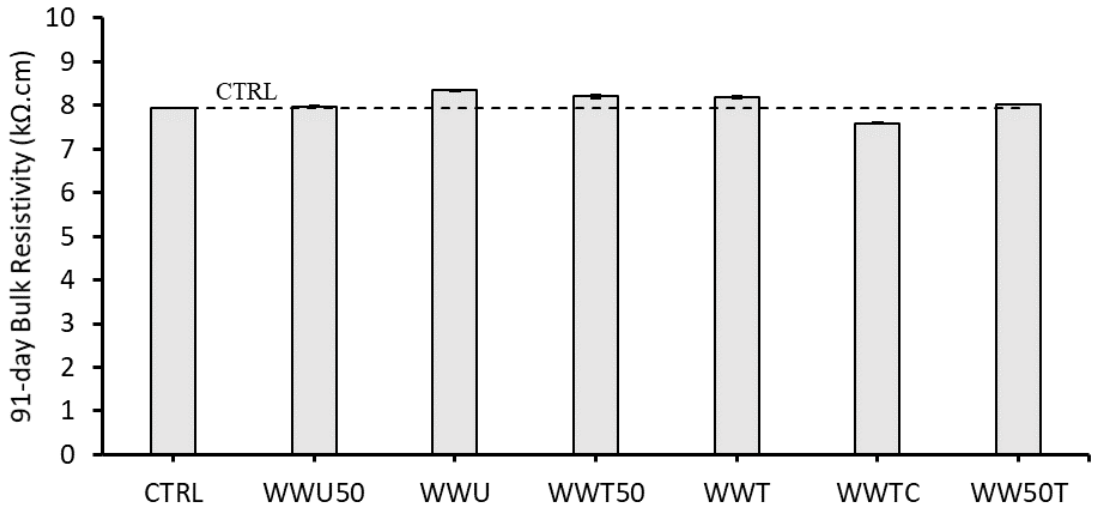

Figure 4.25 91-day Bulk Resistivity Test Results of Concrete Specimens

4.3.3.3 Comparison of Surface and Bulk Resistivity Test Results

Despite the differences in the magnitude of the test results between the bulk and surface resistivity tests, the two test results showed a distinct similarity. Figure 4.26 shows the correlation between the bulk and surface resistivity test results. The coefficient of determination (R^2) between the two test results is 0.96. This indicates that there is a good relationship between the two test methods. Moreover, as suggested in the draft of ASTM WK37880 (2013), when the surface resistivity test results were divided by the recommended correction factor (1.95), the values were closer to the bulk resistivity test results. Figure 4.27 and Figure 4.28 provide a comparison between the bulk resistivity test results and corrected surface resistivity values of concrete specimens at 28-day and 91-day, respectively.

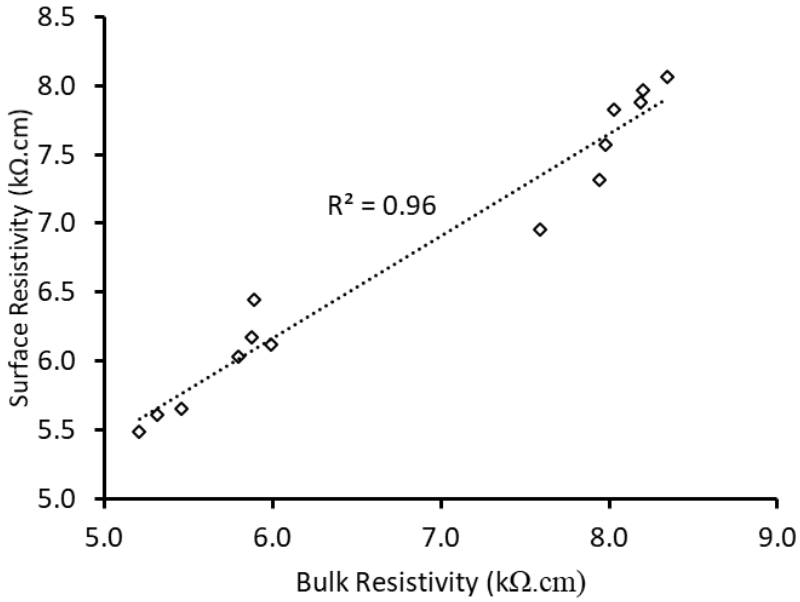

Figure 4.26 Correlation Between The Bulk and Surface Resistivity Test Results

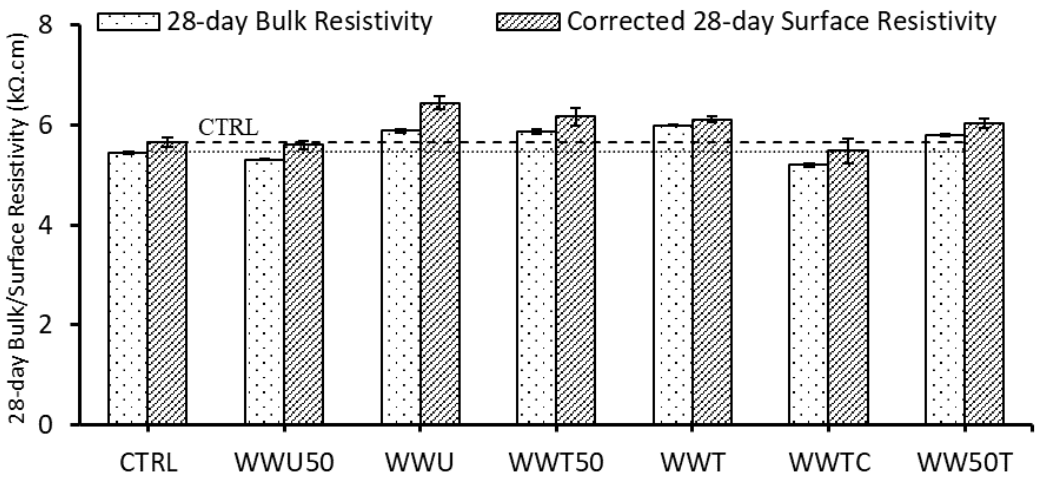

Figure 4.27 Comparison of 28-day Bulk Resistivity and Surface Resistivity Values

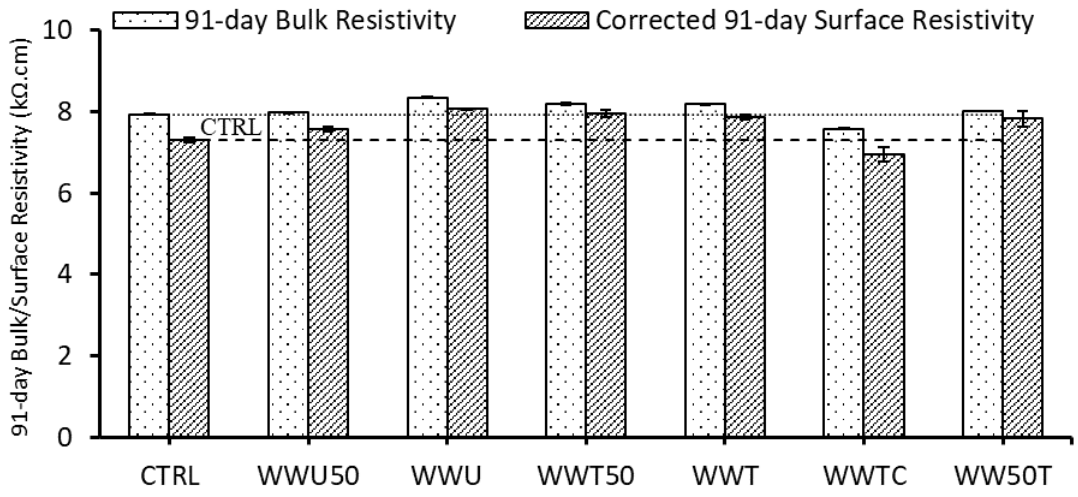

Figure 4.28 Comparison of 91-day Bulk Resistivity and Surface Resistivity Values

4.3.4 Splitting Tensile Strength of Concrete (ASTM C496)

Cylindrical concrete specimens with dimensions of 150 x 300 mm were used for splitting tensile strength tests. The tests were conducted in accordance with ASTM C496 (2017) and a constant loading rate of 1.0 MPa/min was used for all the concrete specimens. It was observed that the fracture line was located through the middle of each specimen. The test results are illustrated in Figure 4.29. The highest and lowest splitting tensile strengths were recorded in CTRL and WWTC, respectively. The splitting tensile strength of concrete mixtures produced with wash water (untreated or CO_2-treated) were between 92% and 100% of the control mixture indicating that the use of wash water (CO_2-treated or otherwise) has little impact on the splitting strength of concrete.

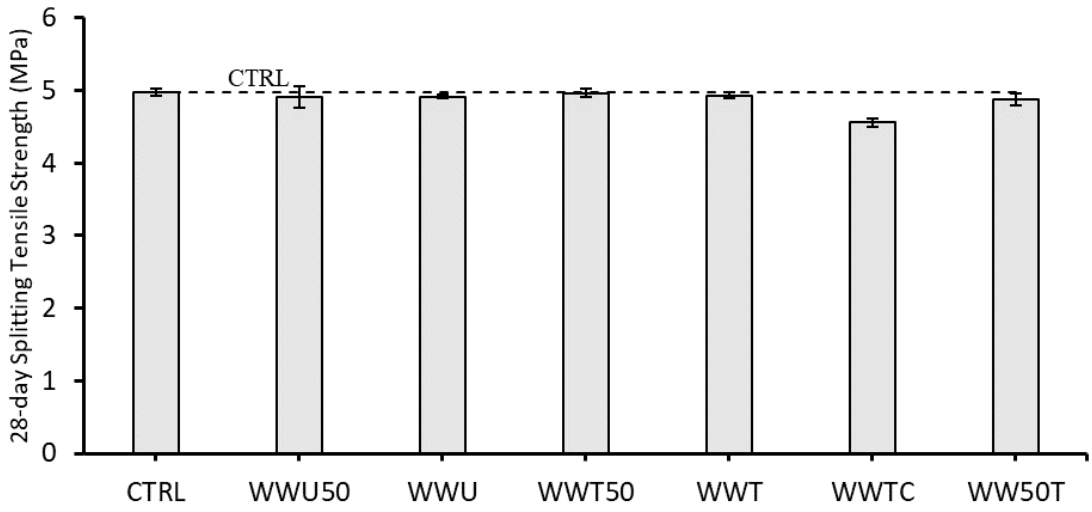

Figure 4.29 28-day Splitting Tensile Strength Test Results of Concrete Specimens

Table 4.8 provides a comparison between the compressive and splitting tensile strength test results. The calculated $f_{st}/\sqrt{f_c}$ values ranged from 0.7 to 0.8 and are slightly higher than the value (0.56) reported in ACI 318R (2014).

Table 4.8 Comparison of the Compressive and Splitting Tensile Strength Test Results

	CTRL	**WWU50**	**WWU**	**WWT50**	**WWT**	**WWTC**	**WW50T**
f_{st} (MPa)	5.0	4.9	4.9	5.0	4.9	4.6	4.9
f_c (MPa)	42.0	42.7	43.3	43.3	42.7	38.7	43.7
$f_{st}/\sqrt{f_c}$	0.8	0.8	0.7	0.8	0.8	0.7	0.7

4.3.5 Flexural Tensile Strength of Concrete (ASTM C78)

The modulus of rupture of concrete prisms (150 x 150 x 530 mm) was determined at 28-days following the procedure per ASTM C78 (2018). The fracture occurred in the middle third of all the tested specimens (that is, the region of constant bending moment). The calculated values of modulus of rupture are shown in Figure 4.30. Note that the values displayed are the average of two prism specimens. The moduli of rupture of CTRL, WWU50, WWT50, and WW50T are approximately equal. WWTC demonstrated the lowest modulus of rupture (87% that of CTRL). All other mixtures have attained comparable results (98-101% compared to CTRL).

It is interesting to analyse the correlation between the results of 28-day compressive strength (f_c) and modulus of rupture (f_r). The comparison of the two results yielded a coefficient of determination (R^2) of 0.86, which is acceptable in general. Table 4.9 presents the comparison between the two test results. The calculated $f_r/\sqrt{f_c}$ values are higher than the value (0.7) expressed by Wood (1992).

Table 4.9 Comparison of the Compressive and Flexural Strength Test Results

	CTRL	WWU50	WWU	WWT50	WWT	WWTC
f_r (MPa)	7.2	7.2	7.0	7.2	7.0	6.2
f_c (MPa)	42.0	42.7	43.3	43.3	42.7	38.7
$f_r/\sqrt{f_c}$	1.1	1.1	1.1	1.1	1.1	1.0

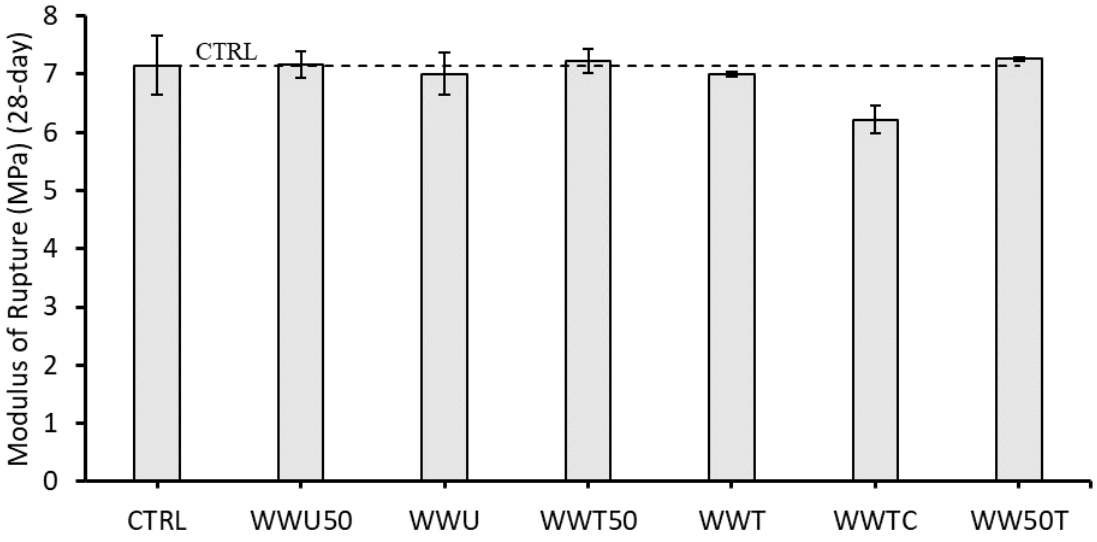

Figure 4.30 28-day Modulus of Rupture of Concrete Specimens

4.3.6 Freeze-Thaw Resistance of Concrete

The freeze-thaw resistance test was conducted on prism specimens with dimensions of 75 x 100 x 405 mm in accordance with ASTM C666 (2015). Fundamental transverse frequency values of the specimens were determined as outlined in ASTM C215 (2014). Due to lack of space in the freeze-thaw apparatus, only 2 prism specimens were used for WWU50 and WW50T. The summary of the test results is presented in Table 4.10. The durability factor (DF) of CTRL was 95% after 300 complete cycles of freezing-and-thawing. Among all the concrete specimens tested, WWTC showed the lowest DF of 92% at the end of the 300 freezing-and-thawing cycles. However, the DF all the concrete mixtures, including WWTC, was above 90% and therefore the resistance of the concrete mixtures to freezing and thawing is acceptable as per the physical requirements for the chemical admixtures outlined in Table 1 of ASTM C494 (2016). Figure 4.31 shows the calculated DF for each concrete mixture.

Table 4.10 Freeze-Thaw Resistance of Concrete Test Results

Mix ID	FTF at 0-cycles (Hz)	FTF after 300-cycles (Hz)	Mass Loss (%)	DF (%)
CTRL	2116	2065	0.2	95
WWU50	2198	2129	0.1	94
WWU	2188	2149	0.1	96
WWT50	2109	2070	0.2	96
WWT	2181	2116	0.2	94
WWTC	2096	2012	0.4	92
WW50T	2139	2065	0.6	93

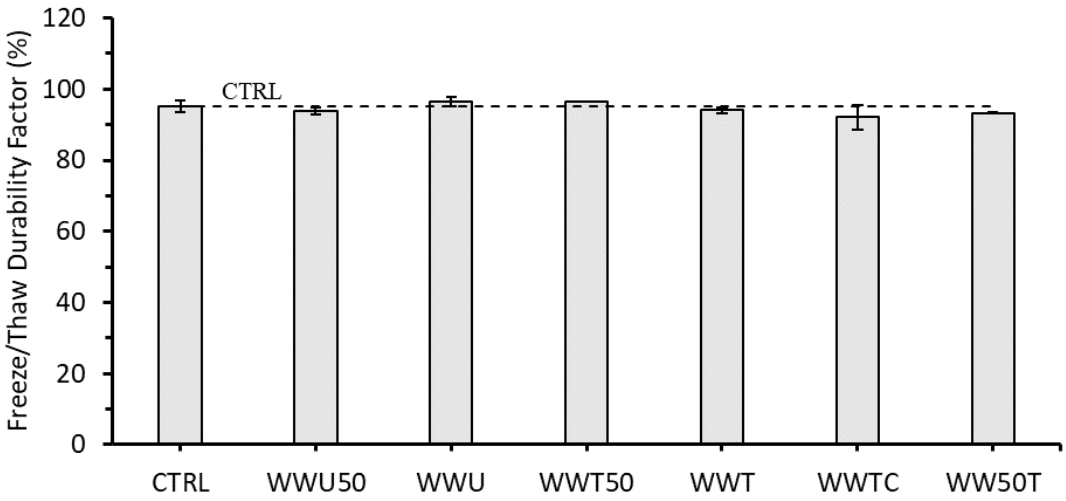

Figure 4.31 Durability Factors of Concrete Specimens

4.4 Overall Performance Analysis of CO_2-Treated Wash Water

4.4.1 Preventing Further Hydration of Wash Water

Based on the chemical analyses, 75% and 100% CO_2-treatments for wash water were successful in hindering the hydration of unreacted cement particles in wash water. 25% and 50% CO_2-treatments slowed down the hydration of unreacted cement in wash water but did not prevent hydration completely.

Although the calculated maximum theoretical CO_2 sequestration extent was 50% for the cement used in this study (Brookfield type GU), 100% CO_2-treatment mineralised 28.7% CO_2 (by weight of cement) only. Since 75% and 100% CO_2-treatment prevented further hydration of wash water, it was hypothesised that CO_2-treatment forms a protective carbonate layer around the cement particles in the wash water and the $CaCO_3$ layer effectively blocks alite and belite phases from hydration.

4.4.1.1 Development of $CaCO_3$ Layer in Wash Water by CO_2-Treatment

Results obtained in sections 4.1.4 and 4.1.5 suggest that 75% and 100% CO_2-treatment levels are more effective in preventing further hydration of wash water compare to other levels of CO_2-treatment. This could be due to the formation of a calcite ($CaCO_3$) layer on suspended cement particles as a result of carbonation (CO_2-treatment) (MacDonald et al. 2020). Figure 4.32 graphically illustrates this concept. This ‘calcite shield’ acts as a protective layer and prevents further hydration of wash water. It is hypothesized, based on the mortar tests, that this calcite layer can be disintegrated mechanically, i.e. by shearing action when it is mixed in a mortar or concrete mixer together with aggregates. As such,

the unreacted cement component of the solids in CO_2-treated wash water can contribute to strength gain in mortar or concrete mixtures.

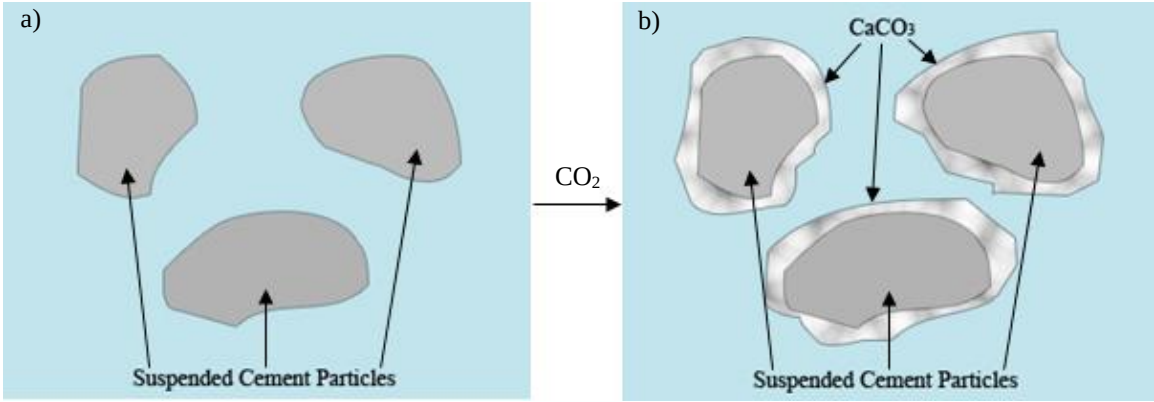

Figure 4.32 Suspended Cement Particles a) before and b) after CO_2-Treatment

4.4.2 Cementitious Contribution of the Solids in CO_2-Treated Wash Water

The results of mortar tests suggest that there is some cementitious value of the solids in wash water even after carbonation. This could be the result of the limestone acting as a filler or reacting with the aluminate phases, both of which have been found to contribute to strength in Portland-limestone cements (Matschei et al. 2007; MacDonald et al. 2020). However, it could also indicate that any unreacted cement that remains after CO_2-treatment hydrates when it is incorporated in mortar or concrete. It is possible that the 'calcite shield' that forms around the unreacted cement during treatment is broken by the shearing action (when it is later mixed in mortar or concrete) and, as a result, the solids in the CO_2-treated wash water contribute to strength development of mortar or concrete mixtures. However, this hypothesis needs to be tested. The mortar and concrete test data also demonstrate that the cementitious contribution played by the solids in the treated wash water becomes more

apparent at later ages The efficiency factor of the solids in 100% CO_2-treated wash water at 7-day and 28-day were found to be 0.2 and 0.7, respectively.

This possibility of reducing the cement content of mixtures would enhance the environmental and economic benefits of using CO_2-treated wash water.

4.4.3 Optimum Level of CO_2-Treatment

An optimum level of carbonation refers to the CO_2 sequestration extent that is sufficient to prevent further hydration of wash water and to maximise the amount of unreacted cement particles in the wash water. On the basis of the results obtained from Phase 1 (chemical analysis) of this study, 75% and 100% CO_2-treatment levels successfully blocked further hydration of wash water.

Determination of the actual optimum level of CO2-treatment is a complex process involving the preparation of several concrete mixtures with various levels of wash water that have been treated with various levels of CO_2. Considering the time limitations of this study, the maximum CO_2-treatment level (28.7% CO_2 uptake by weight of cement) was used in this study.

4.4.4 Fresh and Hardened Properties of Concrete Produced with CO_2-Treated Wash Water

The results of the mortar and concrete tests evidently prove that the use of CO_2-treated wash water as mixing water is not detrimental to any concrete properties. A higher dosage of SP is usually required to achieve an equivalent workability when tap water is completely

replaced with 100% CO_2-treated wash water. The air content was also not affected by the replacement of tap water with CO_2-treated wash water, considering the variability of the test results.

The mortar and concrete mixtures produced with CO_2-treated wash water, with the exception of mixtures with partial cement reduction, demonstrated comparable or better performance compared to the control mixtures. In some cases, the performance of the mixtures with partial cement reduction was also comparable to the control mixtures.

The higher degree of strength improvement that was observed in mortar mixtures as a result of replacement of tap water with CO_2-treated wash water were not apparent in concrete mixtures. However, given the inherent variability of concrete properties, a partial reduction of cement content of concrete mixtures is possible without significantly affecting any concrete properties. This supports the environmental and economic benefits of using CO_2-treated wash water.

This study did not consider the variability of wash water, i.e. there were no SCM in the wash water specimens used for this study. However, SCMs are widely incorporated in concrete. Therefore, further study is required to examine the performance of wash water that consist of one or more SCMs.

Chapter 5. Conclusions and Recommendations

This study was initiated with the aim of evaluating the potential of using CO_2-treated wash water as mixing water in concrete. The latter part of this chapter outlines the recommendations for future studies to acquire more in-depth knowledge of this area of research.

5.1 Conclusions

The following conclusion can be drawn on the basis of the results obtained during the course of this study.

5.1.1 Effectiveness of CO_2 Treatment on Prevention of Hydration of Wash Water

Based on the XRD and bound water analysis, 75 and 100% CO_2-treatments were effective in preventing hydration of any unreacted cement in the solids component of the CO_2-treated wash water. The performance of 50% CO_2-treatment was also tolerable but did not hinder the hydration of wash water completely.

5.1.2 Strength of Mortars Produced with Untreated and CO_2-treated Wash Water

Mortar mixture produced with 100% CO_2-treated wash water achieved the highest 28-day compressive strength. Mortar mixture prepared with untreated wash water showed higher compressive strengths at 1-day and 7-day compared to other mortars. But the strength gain with age demonstrated by the mortar mixture produced with 100% CO_2-treated was superior to all other mortar mixtures.

5.1.3 Fresh Concrete Properties

The air content of concrete was not significantly affected when wash water (untreated or CO_2-treated) was used as mixing water.

Dosage of SP was adjusted in each concrete mixture to achieve a slump in the acceptable range (100-150 mm). A dosage of 300 ml/ 100 kg of cement SP (Euclid™ Plastol 6400) was used for the control mixture, whereas the required dosage was 450 ml/ 100 kg of cement for the concrete mixture with 100% CO_2-treated wash water to match the slump of the control mixture.

5.1.4 Hardened Concrete Properties

- None of the properties of hardened concrete was impaired by the use of CO_2-treated wash water as mixing water. In fact, the highest 7-day, 28-day, and 91-day compressive strengths were achieved by the concrete mixtures produced with CO_2-treated wash water.
- Both surface and bulk resistivity of the concrete mixtures produced with 100% CO_2-treated wash water was comparable to the control mixture.
- Results obtained from the splitting tensile strength and flexural strength tests show that the performance of all concrete mixtures, except those produced with reduced cement content, is equivalent to or better than the control mixture.
- Freeze-thaw resistance tests also demonstrated a similar conclusion that the performance of all concrete mixtures, including the one with reduced cement content, are comparable to the control mixture.

- In summary, the hardened concrete properties that are considered for this study were not adversely affected when CO_2-treated wash water was used as mixing water. Some properties such as compressive strength, especially at later ages, bulk and surface resistivity were improved as a result of incorporating CO_2-treated wash water.

5.1.5 Contribution of CO_2-treated Wash Water in Strength Development

Usage of CO_2-treated wash water as mixing water demonstrated an extensive strength gaining at later ages in both mortar and concrete mixtures. The results of mortar analysis carried out with different W/C ratios suggest that the solids in CO_2-treated wash water can be considered as a binder. The efficiency factor of the solids in 100% CO_2-treated wash water was 0.2 and 0.7 at 7-day and 28-day, respectively.

5.1.6 Conformity of CO_2-Treated Wash Water with ASTM C1602

- CO_2-treated wash water (both 50% and 100%) achieved a 7-day compressive strength more than 90% of control mixture. Hence, CO_2-treated wash water satisfies the performance requirement outlined in ASTM C1602 (2018).
- The concentration of chloride ions in 100% CO_2-treated wash water (30 ppm) was below the optional limit of 500 ppm.
- The concentration of sulphate ions in 100% CO2-treated wash water (1,612 ppm) was less than the optional limit of 3,000 ppm.
- Alkali content (Na_2O Equivalent) of 100% CO_2-treated wash water (566 ppm) was below the optional limit of 600 ppm.

- Total suspended solids (TSS) content of 100% CO_2-treated wash water (~185,000 ppm) was above the optional limit of 50,000 ppm.

5.2 Recommendations

- Although some of the fresh concrete properties such as setting time (using penetrometer) and slump-retention were scheduled to be examined at the final phase of this research programme, these scheduled tests were not conducted due to laboratory closures caused by the pandemic. It is highly recommended that setting time and slump-retention tests for concrete mixtures produced with wash water (untreated or CO2-treated) be carried out in future studies.
- Drying shrinkage test (ASTM C596) is one of the requirements for validating the potential for considering solids in wash water as a type S (specific performance) chemical admixture as outlined in ASTM C494 (2016). Hence, it is recommended to conduct drying shrinkage tests on concrete mixtures produced with wash water (untreated or CO_2-treated) in future studies.
- Wash water specimens used in this study were prepared in-house and consist of water and Portland cement only; however, concrete wash water effluent from ready-mix concrete plants often contains other materials such as chemical and/or mineral admixtures and fine aggregate. Therefore, it is highly recommended to consider this variability of wash water in future studies.
- From the results obtained from the compressive strengths tests of concrete, it was observed that the use of CO_2-treated wash water as mixing water promotes strength

development at later ages. Consequently, it is recommended to consider 91-day compressive strength for mortar mixtures as well.

- The air content of hardened concrete was not determined in this study. It is advisable to measure the air contents of hardened concrete to determine whether air-void parameters (e.g. spacing factor and specific surface) are satisfactory.
- A significant amount of alkalis is present in wash water. Despite the fact that 100% CO_2-treatment produce a neutral (pH of 7.0) wash water, it is advisable to consider other durability parameters, such as resistance to alkali-aggregate reaction and sulphate attack.
- A hypothesis was made in this study as CO_2-treatment forms a calcite layer around the cement particles in wash water and the calcite layer breaks through the shearing action during mixing when the CO_2-treated wash water is used as mixing water in concrete. Further testing is required to elucidate this hypothesis. A potential approach is to perform XRD analysis on two different specimens: (i) 100% CO_2-treated wash water specimen which is stored in the roller machine for 7-days, and (ii) 100% CO_2-treated wash water specimen which is stirred in a high-shear mixer (e.g. food blender) immediately after the CO_2-treatment and stored in the roller machine for 7-days. Portlandite (CH) peaks in the X-ray diffractograms might be used to examine the hydration in the wash water specimens.

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Appendix A

Water Quality Analytical Results – December 2019

Chemical Parameters	[1]Units	Guidelines for Canadian Drinking Water Quality	Typical Distribution System Water
Benzene- *found in gasoline and used in industrial processes*	ug/L	5	ND
Carbon Tetrachloride- *produced while manufacturing other hydrocarbons*	ug/L	2	ND
1,2 Dichlorobenzene- *found in paint removers and degreasers*	ug/L	200	ND
1,4 Dichlorobenzene- *found in paint removers and degreasers*	ug/L	5	ND
1,2 Dichloroethane- *used in preparation of poly vinyl chloride (PVC)*	ug/L	5	ND
Dichloromethane- *volatile liquid used in paint strippers, degreasers and aerosols*	ug/L	50	ND
Ethyl Benzene- *found in gasoline used to make plastics*	ug/L	140	ND
Tetrachloroethylene- *solvent used in dry cleaning and metal cleaning industries*	ug/L	30	ND
Total Trihalomethanes- *by-products associated with chlorine disinfection*	ug/L	100	0-50
Total Xylenes- found in gasoline and used to make consumer products	ug/L	90	ND
Toluene- *found in gasoline, solvents and glues*	ug/L	60	ND
Trichloroethylene- *metal parts degreaser and dry cleaning solvent*	ug/L	5	ND
Vinyl Chloride- *synthetic chemical with no known natural sources*	ug/L	2	ND
Benzo(a)pyrene- *found in creosote and cigarette smoke*	ug/L	0.01	ND
Pentachlorophenol- *used in pesticides and wood preservatives*	ug/L	60	ND
Inorganic Parameters - *a range of materials that are both naturally occurring and artificially produced*			
Alkalinity- *the capacity of water to neutralize acids*	mg/L	~	90
Aluminium- *inorganic metallic element*	mg/L	0.1	0.023
Antimony- *element used in metal manufacturing, historically mined in N.B.*	ug/L	6	<0.1
Arsenic- *can occur naturally or come from industrial effluents*	ug/L	10	<1.0
Barium- *occurs naturally and is produced by industry*	mg/L	1	0.029
Boron- *naturally occurring in over 80 minerals*	mg/L	5	0.009
Bromide- *natural element, often associated with salt deposits*	mg/L	~	<0.05
Cadmium- *metal plating and batteries*	ug/L	5	<0.01
Calcium- *occurs naturally helps produce "hard" water*	mg/L	~	42.4
Chloride- *found in road salts, sea water and processed food*	mg/L	250	33.2
Chromium- *natural metallic element used to plate metal*	mg/L	0.05	<0.001
Conductivity- *measures the waters capacity to carry an electric current*	uS/cm	~	302
Copper- *can stain laundry at levels above Guidelines for Canadian Drinking Water Quality*	mg/L	1	0.01
Fluoride- *occurs naturally in many minerals*	mg/L	1.5	0.09
Iron- *can cause staining in laundry and plumbing*	mg/L	0.3	0.02
Lead- *can be found in older plumbing fixtures, and in solder*	ug/L	10	<0.1
Magnesium- *along with calcium, contributes to forming "hard" water*	mg/L	~	3.46
Manganese- *metal; can cause staining in laundry and plumbing fixtures*	mg/L	0.05	0.007
Nitrate- *often used in inorganic fertilizers*	mg/L	45	0.28
Nitrate / Nitrite- *naturally occurring ions, used in inorganic fertilizers*	mg/L	~	0.28
Nitrite- *naturally occurring, used in food preservatives*	mg/L	3.2	<0.05
pH- *measure of acidity*	pH	6.5 - 8.5	8.2
Potassium- *similar to sodium, essential element , found in potash fertilizer*	mg/L	~	0.92
Selenium- *metal used to make red glass, active ingredient in some shampoo*	ug/L	50	<1.0
Sodium- *found in table salt, road salt and processed food*	mg/L	≤200	12.7
Sulfate- *occurs naturally found in gypsum*	mg/L	500	14
Thallium- *rare metallic element*	ug/L	~	<1.0
Total Hardness- *caused by dissolved minerals primarily calcium and magnesium*	mg/L	[2] See Note	120
Turbidity- *a measure of suspended solids in the water*	NTU	1	<0.1
Uranium- *naturally occurring element*	ug/L	20	0.03
Zinc- *found in some plumbing fixtures and galvanized metal*	mg/L	5	<0.001

[1] Note: mg/L are parts per million; ug/L are parts per billion

[2] Note Public acceptance of hardness varies considerably. Levels up to 100 mg/L are considered "acceptable" with levels greater than 200 mg/L poor but tolerable. Unacceptable levels are greater than 500 mg/L.

Hardness Scale (as per Health Canada)

Soft	0 to <60 mg/L;	0 - 3.5 grains	
Medium hard	60 to <120 mg/L	3.5 - 7.0 grains	***The City of Fredericton's water is medium hard.***
Hard	120 to < 180 mg/L	7.0 - 10.5 grains	
Very hard	180 mg/L & above.	10.5 grains & above	

Manganese commonly occurs in groundwater in New Brunswick. At concentrations greater than 0.15 mg/L, manganese can stain plumbing fixtures and laundry and may cause undesirable taste in beverages. The City of Fredericton's Water Treatment Plants remove manganese through a process of chlorination and filtration.

ND = Not Detected (level below detection limit of instrumentation)

Appendix B

Cement Mill Test Report for Lafarge Portland Cement Type GU

LAFARGE CEMENT

Cement Mill Test Report

Plant:	**Brookfield, Nova Scotia**
Product:	**Portland Cement Type GU**
Manufactured:	**August 2019**

CSA A3001-18 Standard Requirements

CHEMICAL ANALYSIS

Item	Spec limit	Test Result
Rapid Method, X-Ray		
SiO2 (%)	---	19.6
Al2O3 (%)	---	5.5
Fe2O3 (%)	---	2.00
CaO (%)	---	63.3
MgO (%)	5.0 max	1.7
SO3 (%)	3.5 max [1]	4.0
Loss on ignition @ 950 (%)	3.0 (3.5) max [2]	3.7
Loss on ignition @ 550(%)	3.0 max	0.8
Insoluble residue (%)	1.5 max	1.2 [3]
Potential Phase Composition		
C3S (%)	---	57
C2S (%)	---	13
C3A (%)	---	11
C4AF (%)	---	6
CSA A3001-13 Optional Chemical Requirements:		
NaEq (%)		0.97

PHYSICAL ANALYSIS

Item	Spec limit	Test Result
Blaine Fineness (m2/kg)		403
Fineness, Residue passing on a 45 um sieve (%)	72 min	96.2
Fineness, Residue retained on a 45 um sieve (%)	28 max	3.8
Autoclave expansion (%)	1.0 max	0.03
Compressive strength (MPa)		
3 days	14.5 min	30.7
7 days	20.0 min	35.1
28 days	26.5 min	42.3
28 days cv	8.0 max	1.9
Time of setting (minutes)		
Vicat Initial	45 - 375	107
Mortar Bar Expansion C5 (%)	0.020 max	0.007 [3]

[1] May exceed 3.5% SO3 maximum based on our A3004-C5 results of <0.020% expansion at 14 days.

[2] May exceed 3.0% LOI maximum based on our LOI at 550C < 3.0 %

[3] Current Production run not available - most recent provided

We certify that the above described cement, at the time of shipment, meets the chemical and physical requirements of applicable Specifications for Type GU
CSA A3001-18 STANDARD SPECIFICATIONS FOR TYPE GU CEMENT;

Certified By:

Rick Camm Quality & Optimization Manager
Tuesday, September 17, 2019

Eastern Canada Region - Brookfield Plant
87 Cement Plant Road, Brookfield, NS
Phone: (902) 673-2281

Appendix C

Mixture Designs of Concrete Mixtures

W/CM	0.45
Total Cem.	400
Water Cont.	180
WW (%)	0
SCMs	0%

Batch Size (l)	80
Euclid Plastol 6400 (ml)	96.0
SP Dosage (ml/100 kg Cem.)	300
MasterAir AE 200 (ml)	10.2
AEA Dosage (ml/100 kg Cem.)	32

Material	ABS	Proportions (kg/m^3)	Density (kg/m^3)	Volume	M/C	Correction (kg/m^3)	Batch (kg)
Port. Cem.		400	3,150	0.13		400.00	32.00
Water		180	1,000	0.18		188.61	15.09
WW		0	1,100	0.00		0.00	0.00
Coarse Agg.	1	1,000	2,700	0.37	0.42	994.26	79.54
Fine Agg.	1.1	691	2,630	0.26	0.68	687.89	55.03
Air Content				0.06			
Total Vol.				1.000		**Total Wt. (kg)**	181.66
Sand/Agg.		40.85		40%		**Theor. Density (kg/m^3)**	2,270.76
Coarse Agg.				60%			

Figure C. 1 Mixture Design for CTRL

W/CM	0.45
Total Cem.	400
Water Cont.	180
WWU (%)	50
SCMs	0%

Batch Size (l)	80
Euclid Plastol 6400 (ml)	112.0
SP Dosage (ml/100 kg Cem.)	350
MasterAir AE 200 (ml)	10.2
AEA Dosage (ml/100 kg Cem.)	32

Material	ABS	Proportions (kg/m^3)	Density (kg/m^3)	Volume	M/C	Correction (kg/m^3)	Batch (kg)
Port. Cem.		400	3,150	0.13		400.00	32.00
Water		90	1,000	0.09		94.28	7.54
WWU		104	1,100	0.09		109.08	8.73
Coarse Agg.	1	1,000	2,700	0.37	0.42	994.26	79.54
Fine Agg.	1.1	678	2,630	0.26	0.68	675.67	54.05
Air Content				0.06			
Total Vol.				1.000		**Total Wt. (kg)**	181.86
Sand/Agg.		40.42		40%		**Theor. Density (kg/m^3)**	2,273.29
Coarse Agg.				60%			

Figure C. 2 Mixture Design for WWU50

W/CM	0.45
Total Cem.	400
Water Cont.	180
WWU (%)	100
SCMs	0%

Batch Size (l)	80
Euclid Plastol 6400 (ml)	160.0
SP Dosage (ml/100 kg Cem.)	500
MasterAir AE 200 (ml)	10.2
AEA Dosage (ml/100 kg Cem.)	32

Material	ABS	Proportions (kg/m^3)	Density (kg/m^3)	Volume	M/C	Correction (kg/m^3)	Batch (kg)
Port. Cem.		400	3,150	0.13		400.00	32.00
Water		0	1,000	0.00		0.00	0.00
WWU		208	1,100	0.19		218.11	17.45
Coarse Agg.	1	1,000	2,700	0.37	0.42	994.26	79.54
Fine Agg.	1.1	666	2,630	0.25	0.68	663.46	53.08
Air Content				0.06			
Total Vol.				1.000		**Total Wt. (kg)**	182.07
Sand/Agg.		39.98		40%		**Theor. Density (kg/m^3)**	2,275.82
Coarse Agg.				60%			

Figure C. 3 Mixture Design for WWU

W/CM	0.45
Total Cem.	400
Water Cont.	180
WWT (%)	50
SCMs	0%

Batch Size (l)	80
Euclid Plastol 6400 (ml)	128.0
SP Dosage (ml/100 kg Cem.)	400
MasterAir AE 200 (ml)	10.2
AEA Dosage (ml/100 kg Cem.)	32

Material	ABS	Proportions (kg/m^3)	Density (kg/m^3)	Volume	M/C	Correction (kg/m^3)	Batch (kg)
Port. Cem.		400	3,150	0.13		400.00	32.00
Water		90	1,000	0.09		94.52	7.56
WWT		111	1,130	0.10		116.79	9.34
Coarse Agg.	1	1,000	2,700	0.37	0.40	994.06	79.52
Fine Agg.	1.1	669	2,630	0.25	0.63	665.55	53.24
Air Content				0.06			
Total Vol.				1.000		**Total Wt. (kg)**	181.67
Sand/Agg.		40.07		40%		**Theor. Density (kg/m^3)**	2,270.92
Coarse Agg.				60%			

Figure C. 4 Mixture Design for WWT50

W/CM	0.45
Total Cem.	400
Water Cont.	180
WWT (%)	100
SCMs	0%

Batch Size (l)	80
Euclid Plastol 6400 (ml)	144.0
SP Dosage (ml/100 kg Cem.)	450
MasterAir AE 200 (ml)	10.2
AEA Dosage (ml/100 kg Cem.)	32

Material	ABS	Proportions (kg/m^3)	Density (kg/m^3)	Volume	M/C	Correction (kg/m^3)	Batch (kg)
Port. Cem.		400	3,150	0.13		400.00	32.00
Water		0	1,000	0.00		0.00	0.00
WWT		222	1,130	0.20		232.80	18.62
Coarse Agg.	1	1,000	2,700	0.37	0.42	994.26	79.54
Fine Agg.	1.1	647	2,630	0.25	0.68	643.87	51.51
Air Content				0.06			
Total Vol.				1.000		**Total Wt. (kg)**	181.67
Sand/Agg.		39.27		40%		**Theor. Density (kg/m^3)**	2,270.93
Coarse Agg.				60%			

Figure C. 5 Mixture Design for WWT

W/CM	0.45
Total Cem.	400
Water Cont.	180
WWT (%)	100
SCMs	0%

Batch Size (l)	80
Euclid Plastol 6400 (ml)	85.4
SP Dosage (ml/100 kg Cem.)	300
MasterAir AE 200 (ml)	9.1
AEA Dosage (ml/100 kg Cem.)	32

Material	ABS	Proportions (kg/m^3)	Density (kg/m^3)	Volume	M/C	Correction (kg/m^3)	Batch (kg)
Port. Cem.		400	3,150	0.11		355.64	28.45
Water		0	1,000	0.00		0.00	0.00
WWT		222	1,130	0.20		233.66	18.69
Coarse Agg.	1	1,000	2,700	0.37	0.40	994.06	79.52
Fine Agg.	1.1	684	2,630	0.26	0.63	680.42	54.43
Air Content				0.06			
Total Vol.				1.000		**Total Wt. (kg)**	181.10
Sand/Agg.		40.60		40%		**Theor. Density (kg/m^3)**	2,263.77
Coarse Agg.				60%			

Figure C. 6 Mixture Design for WWTC

W/CM	0.45
Total Cem.	400
Water Cont.	180
WW50T (%)	100
SCMs	0%

Batch Size (l)	80
Euclid Plastol 6400 (ml)	160.0
SP Dosage (ml/100 kg Cem.)	500
MasterAir AE 200 (ml)	10.2
AEA Dosage (ml/100 kg Cem.)	32

Material	ABS	Proportions (kg/m^3)	Density (kg/m^3)	Volume	M/C	Correction (kg/m^3)	Batch (kg)
Port. Cem.		400	3,150	0.13		400.00	32.00
Water		0	1,000	0.00		0.00	0.00
WW50T		215	1,115	0.19		226.08	18.09
Coarse Agg.	1	1,000	2,700	0.37	0.40	994.06	79.52
Fine Agg.	1.1	656	2,630	0.25	0.63	653.21	52.26
Air Content				0.06			
Total Vol.				1.000		**Total Wt. (kg)**	181.87
Sand/Agg.		39.62		40%		**Theor. Density (kg/m^3)**	2,273.35
Coarse Agg.				60%			

Figure C. 7 Mixture Design for WW50T

Appendix D

Raw XRD Plots

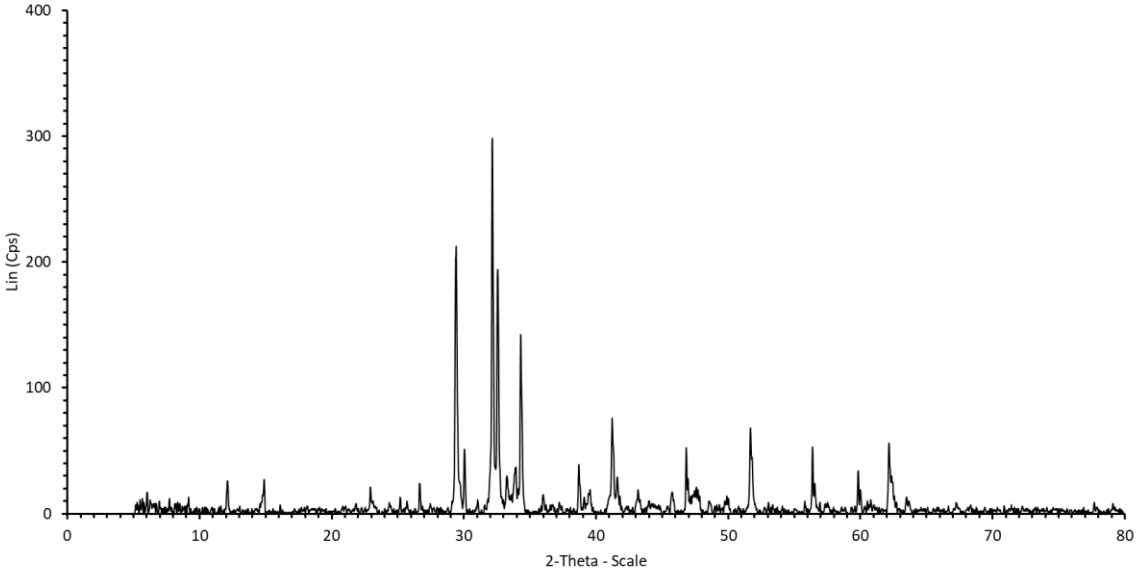

Figure D. 1 X-Ray Diffractogram Obtained for Portland Cement

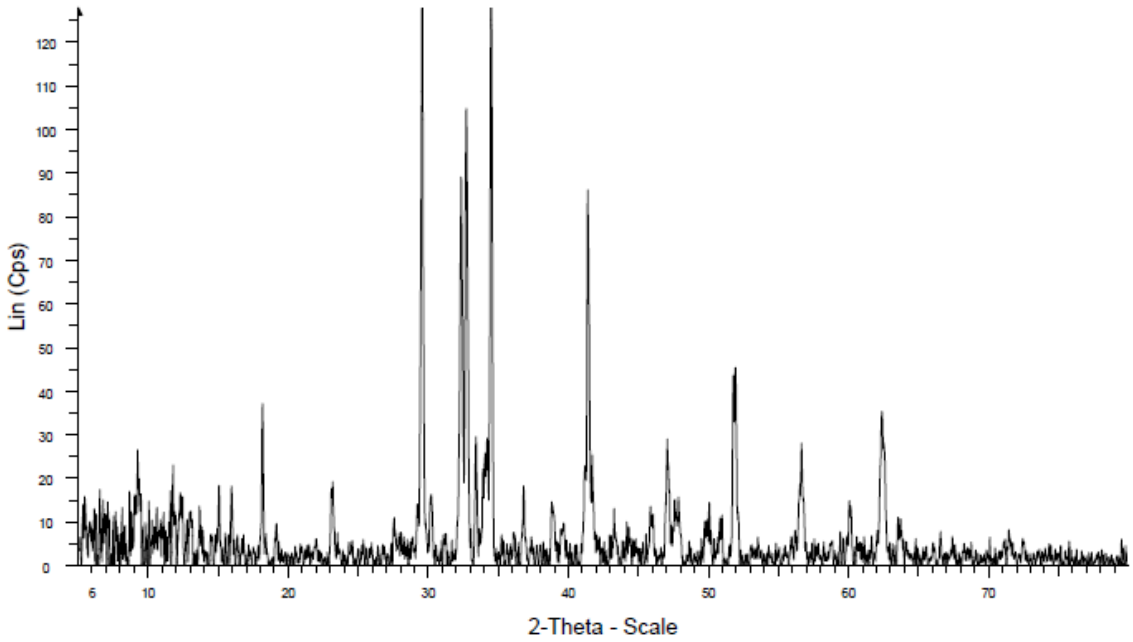

Figure D. 2 X-Ray Diffractogram Obtained for WWU0H

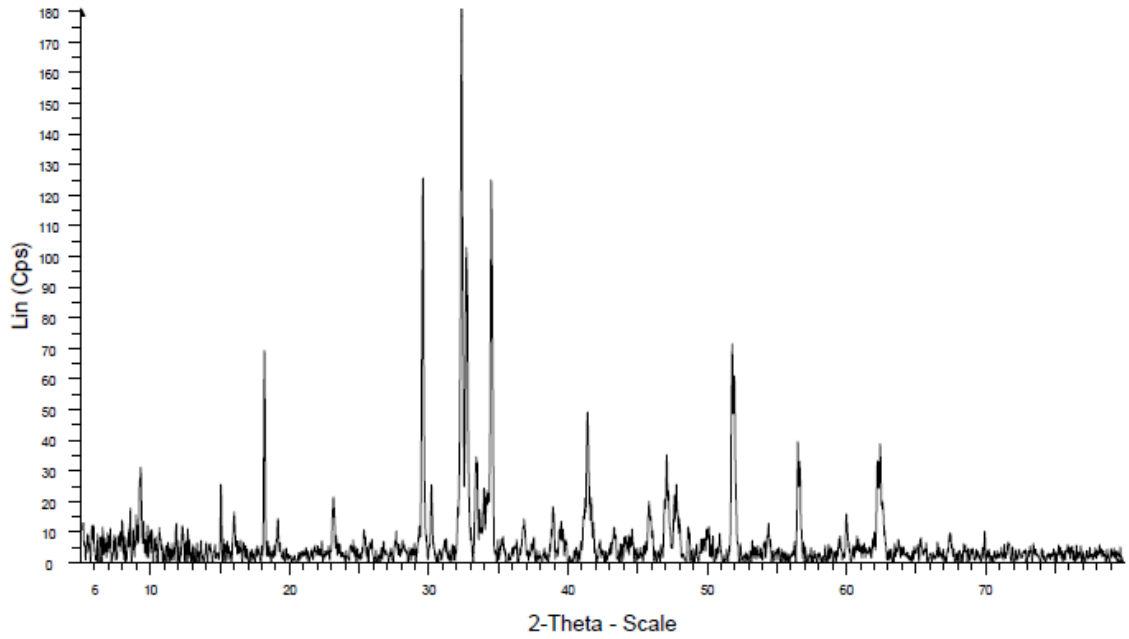

Figure D. 3 X-Ray Diffractogram Obtained for WWU1H

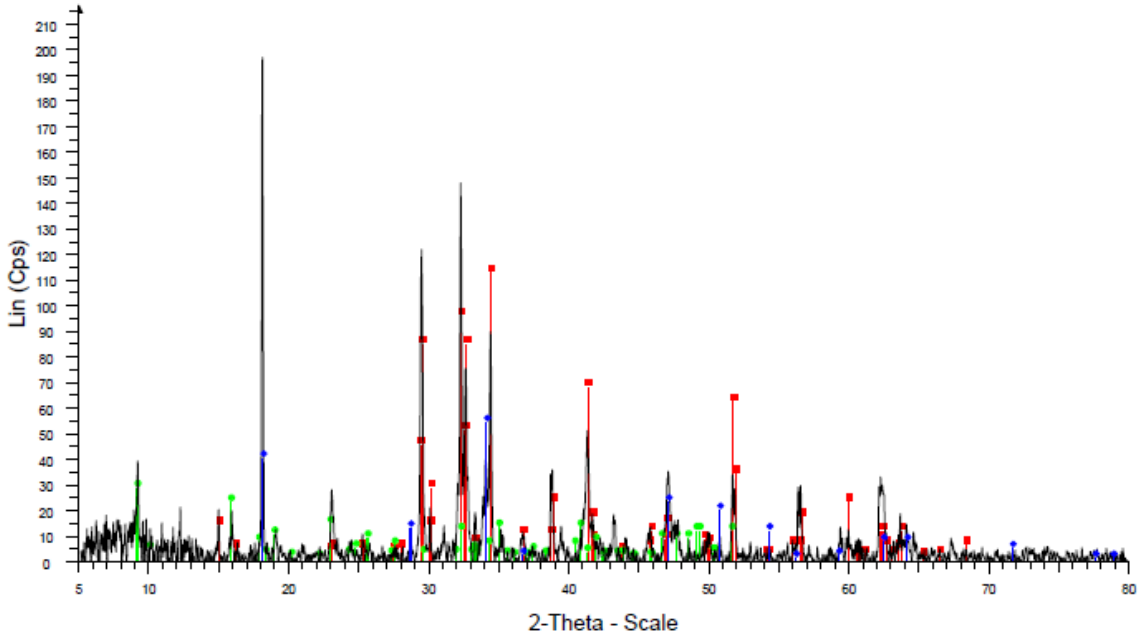

Figure D. 4 X-Ray Diffractogram Obtained for WWU3H

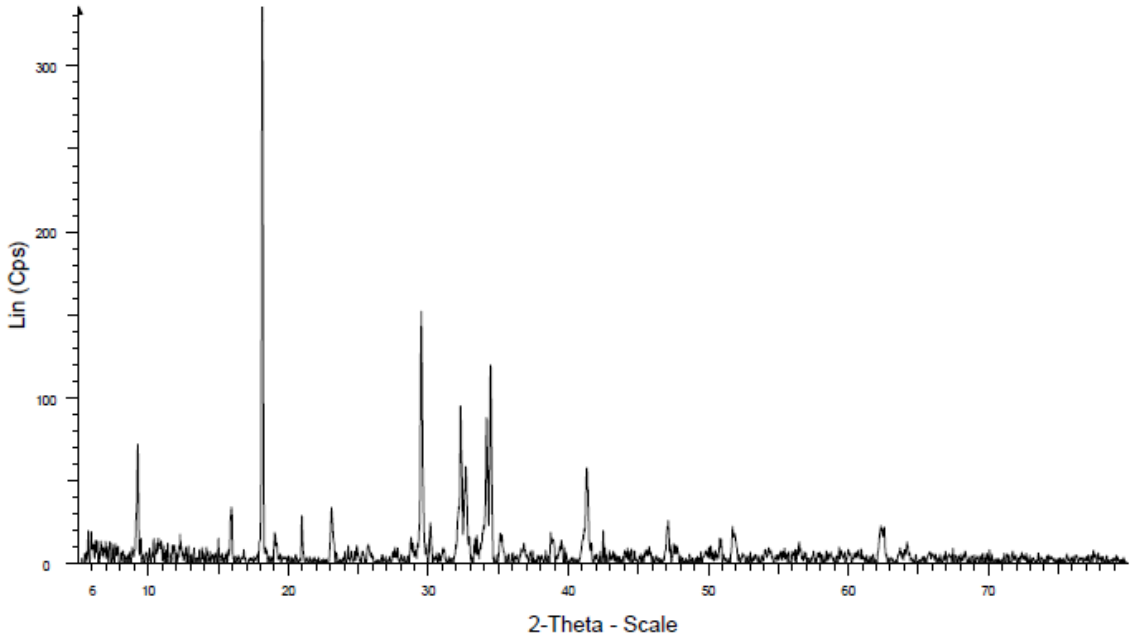

Figure D. 5 X-Ray Diffractogram Obtained for WWU1D

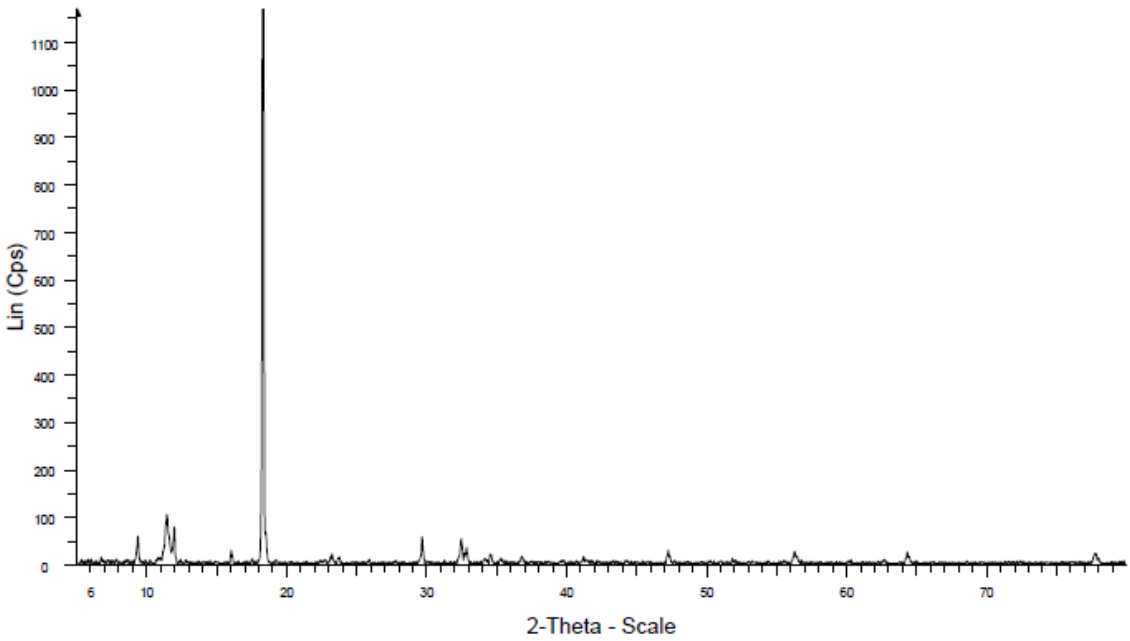

Figure D. 6 X-Ray Diffractogram Obtained for WWU3D

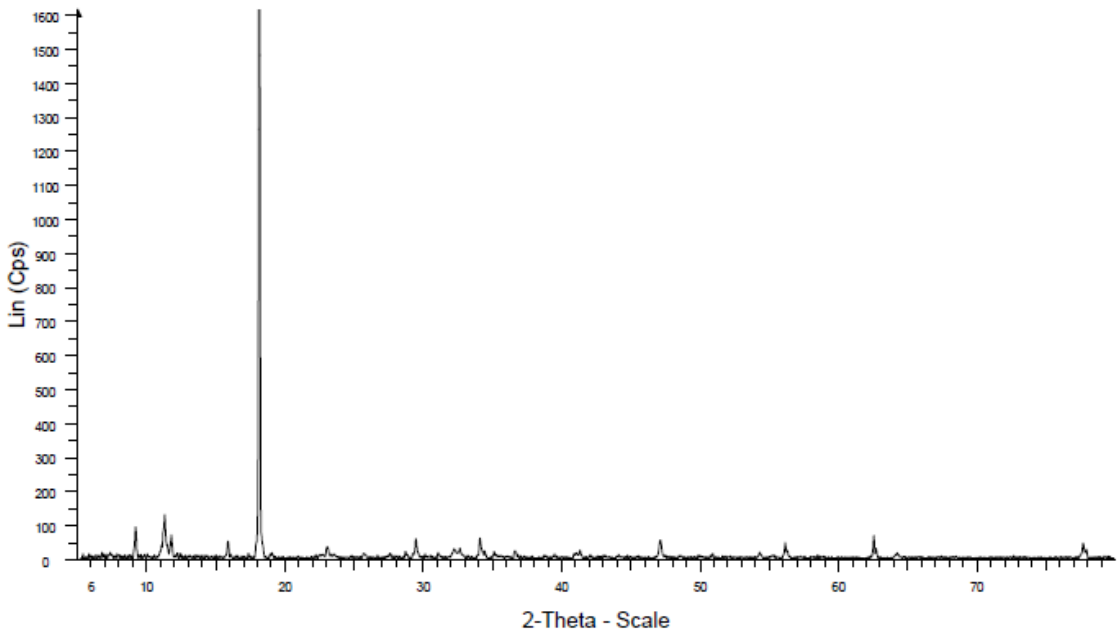

Figure D. 7 X-Ray Diffractogram Obtained for WWU7D

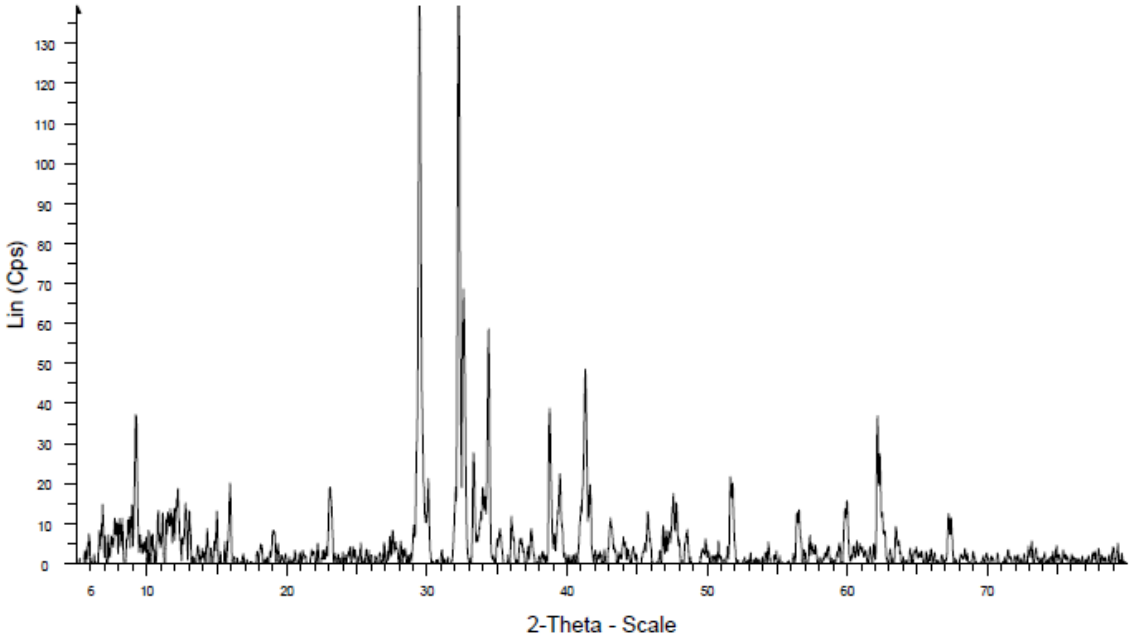

Figure D. 8 X-Ray Diffractogram Obtained for WW25T0H

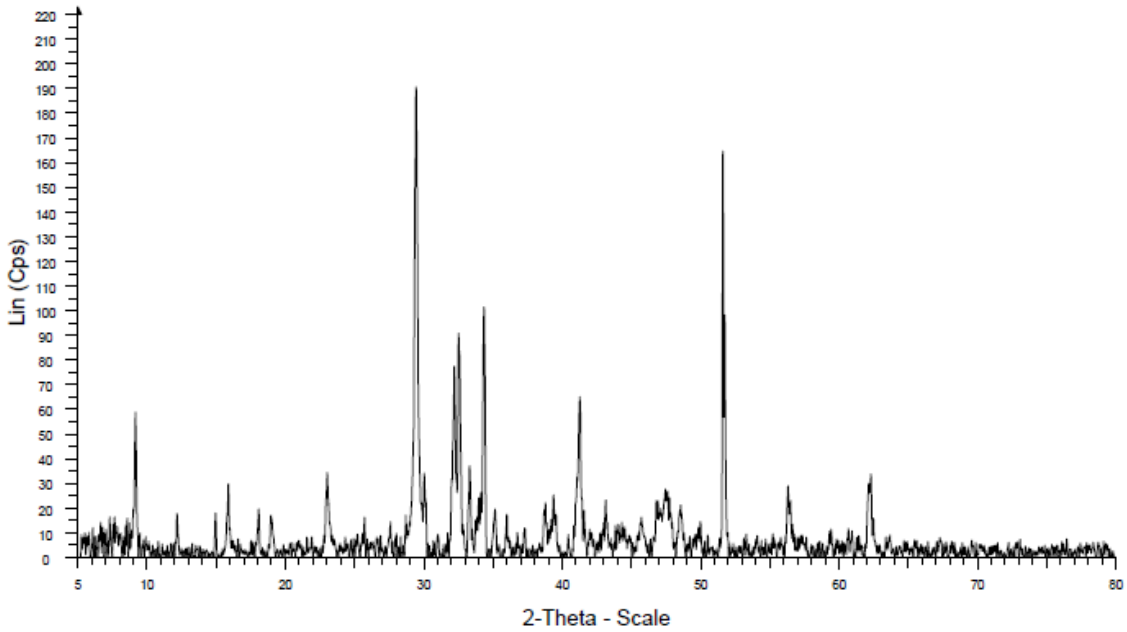

Figure D. 9 X-Ray Diffractogram Obtained for WW25T1H

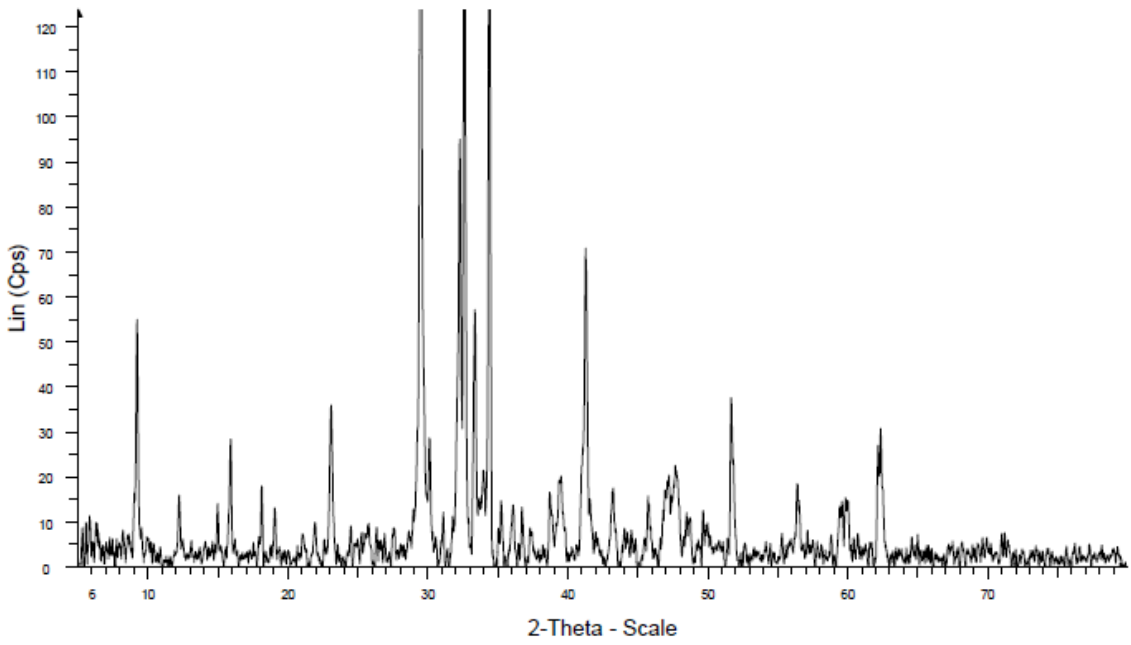

Figure D. 10 X-Ray Diffractogram Obtained for WW25T3H

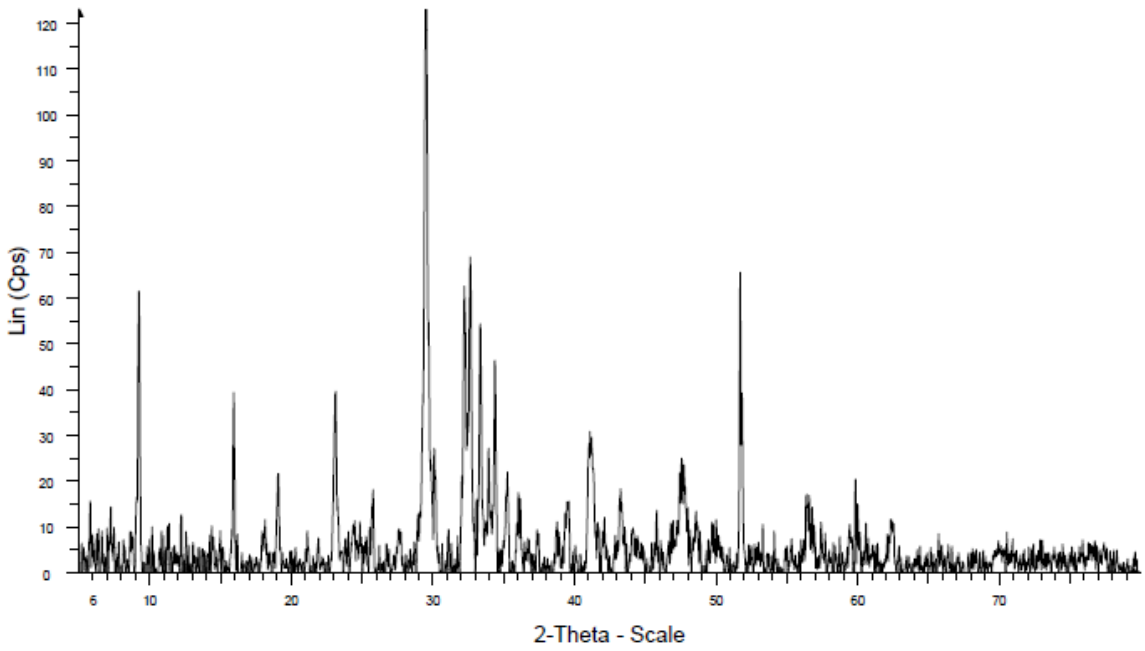

Figure D. 11 X-Ray Diffractogram Obtained for WW25T1D

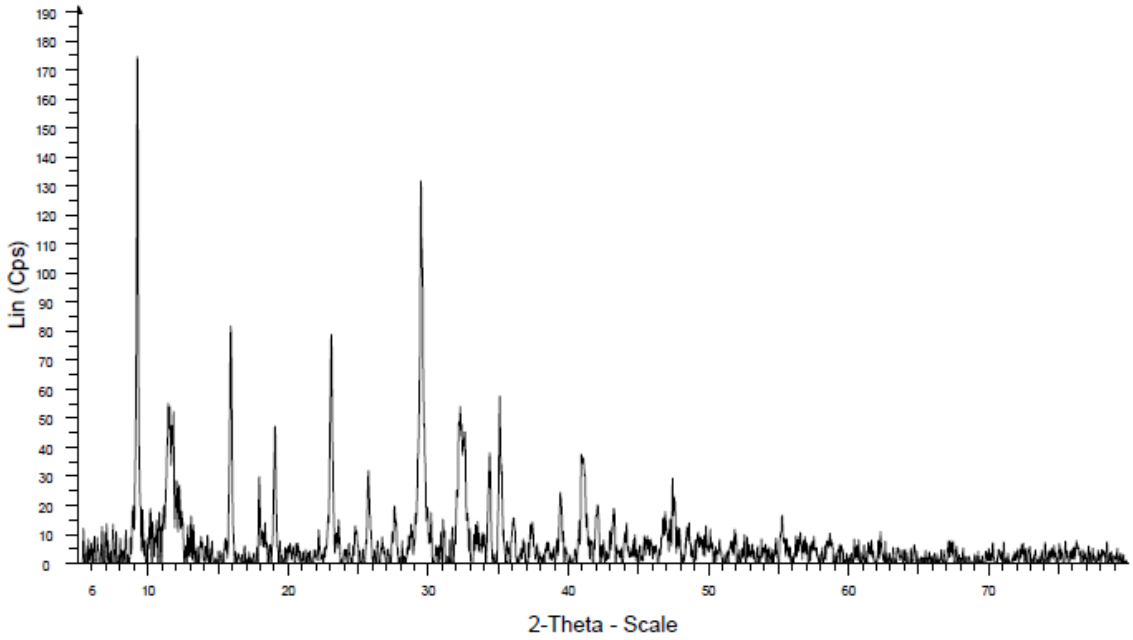

Figure D. 12 X-Ray Diffractogram Obtained for WW25T3D

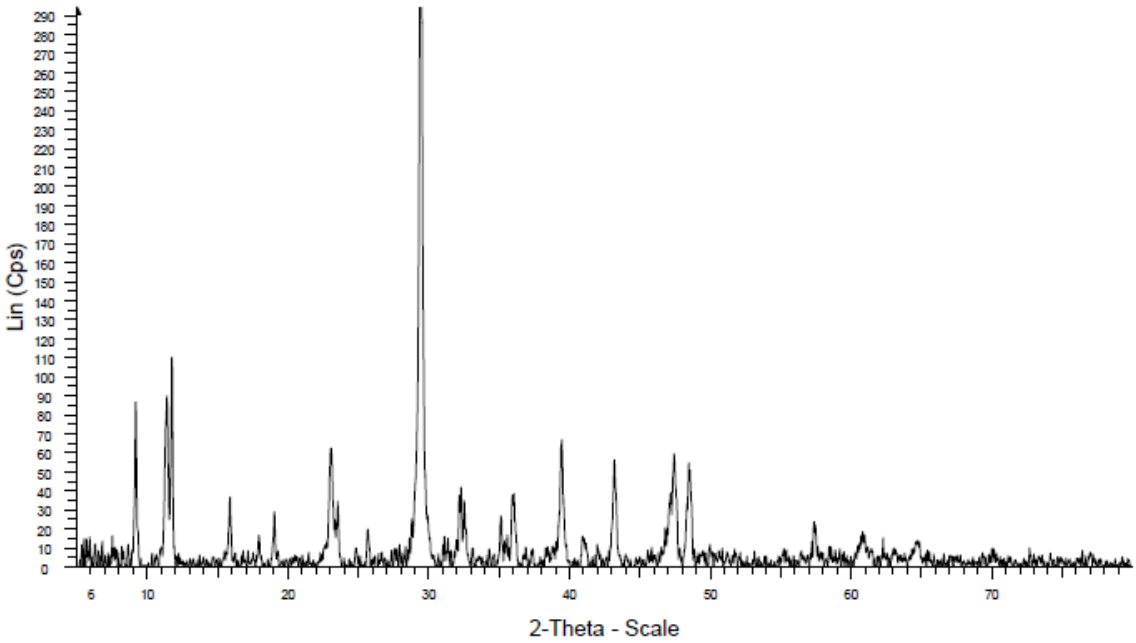

Figure D. 13 X-Ray Diffractogram Obtained for WW25T7D

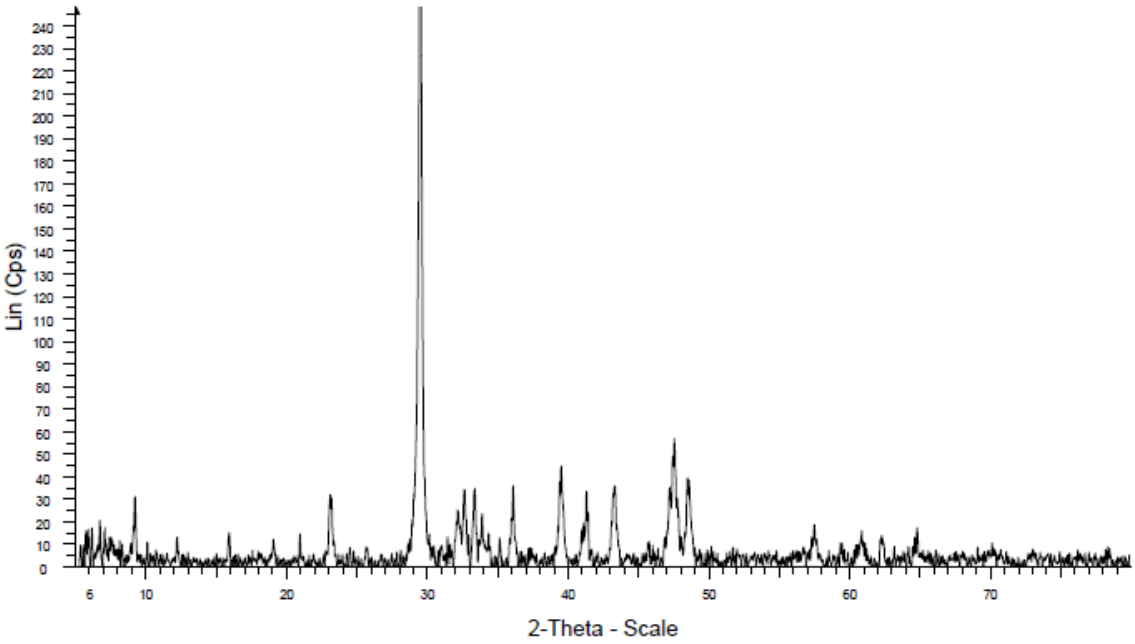

Figure D. 14 X-Ray Diffractogram Obtained for WW50T0H

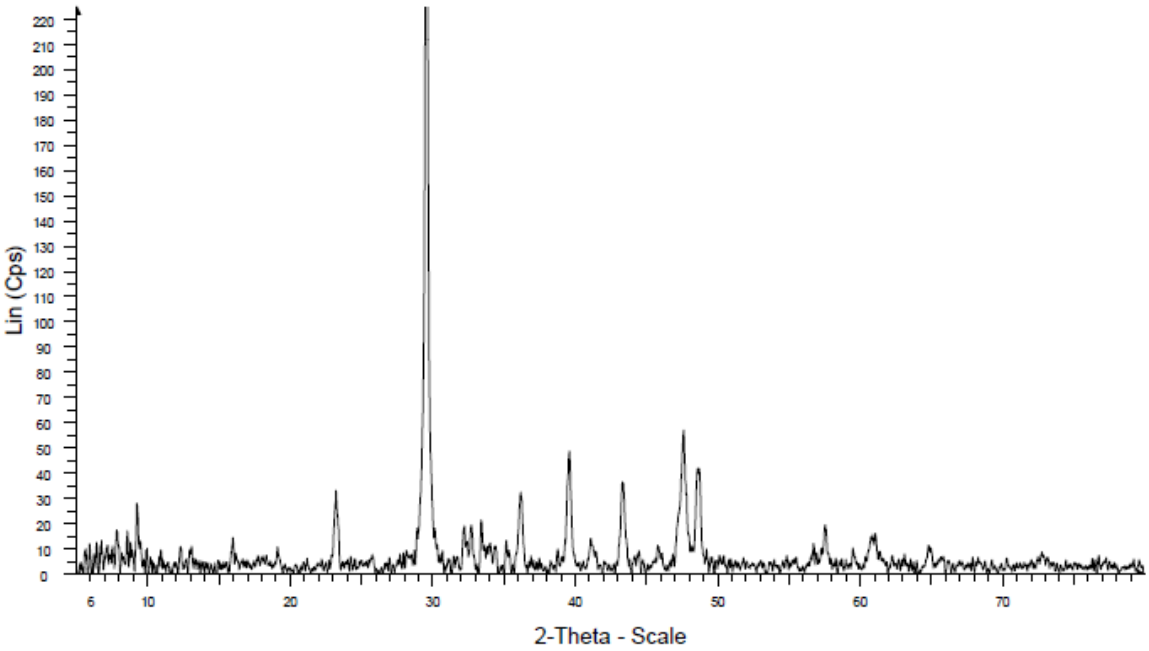

Figure D. 15 X-Ray Diffractogram Obtained for WW50T1H

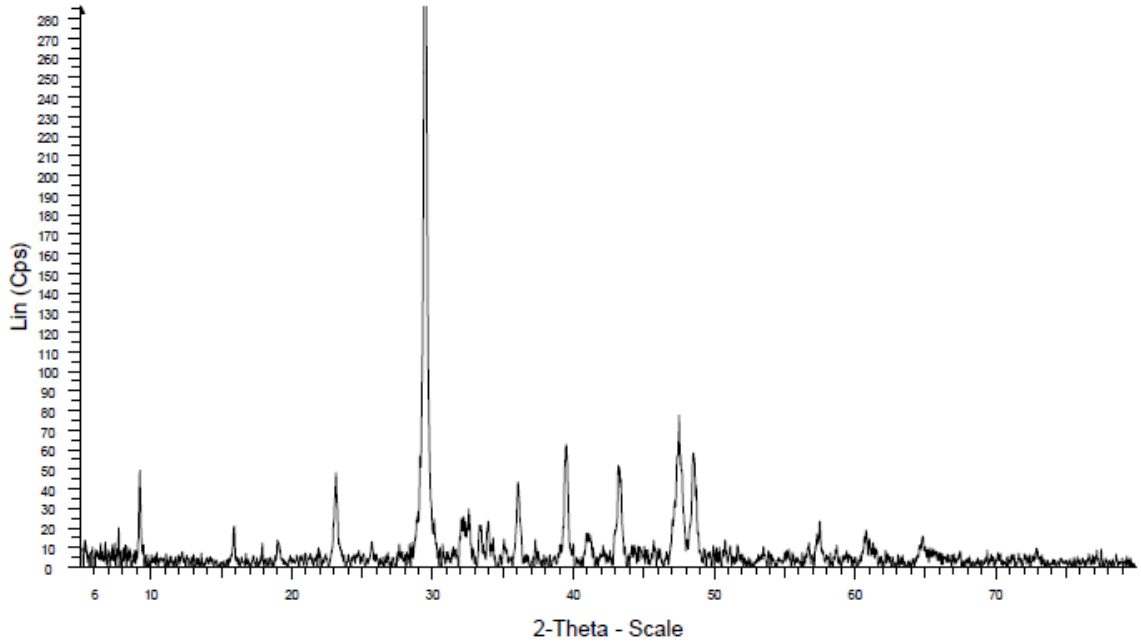

Figure D. 16 X-Ray Diffractogram Obtained for WW50T3H

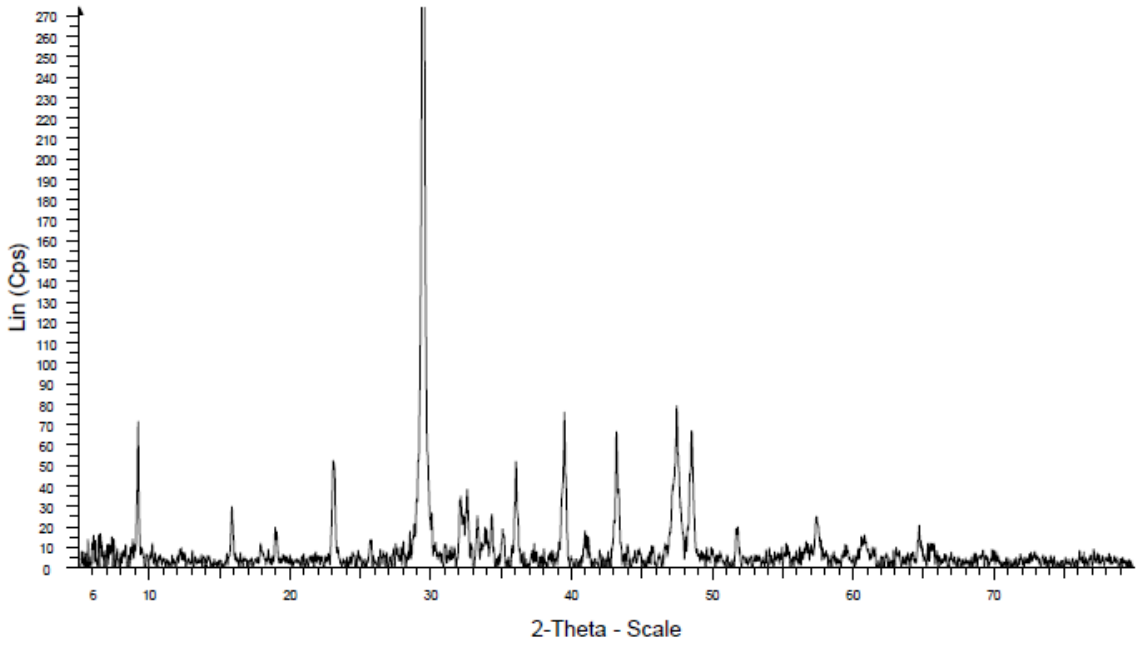

Figure D. 17 X-Ray Diffractogram Obtained for WW50T1D

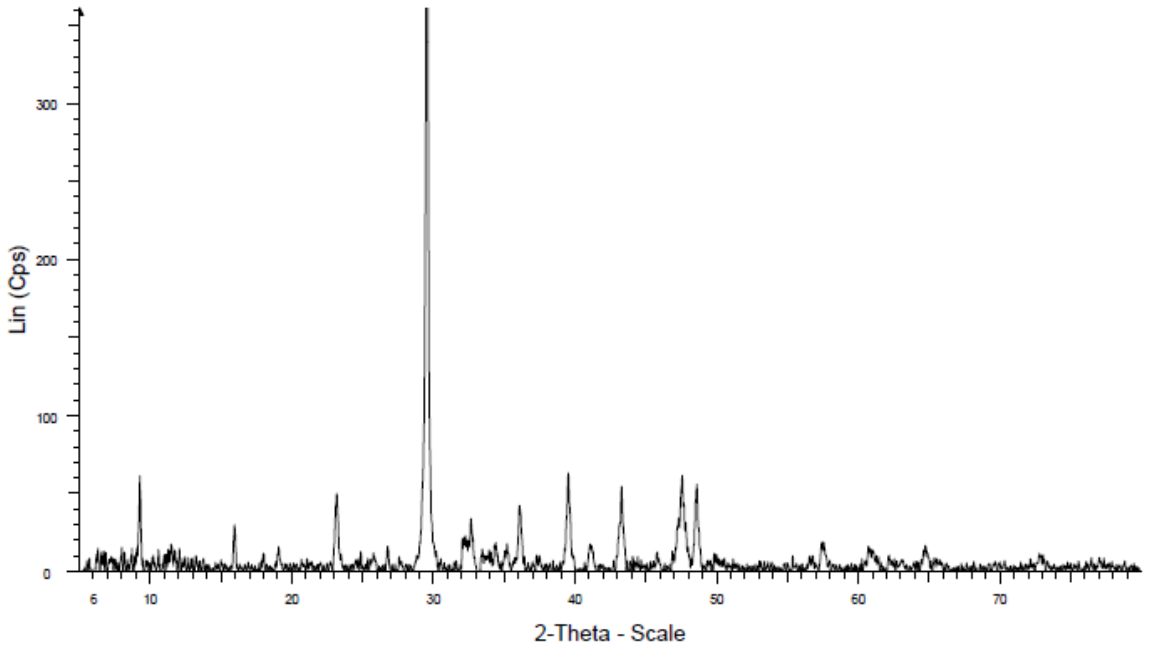

Figure D. 18 X-Ray Diffractogram Obtained for WW50T3D

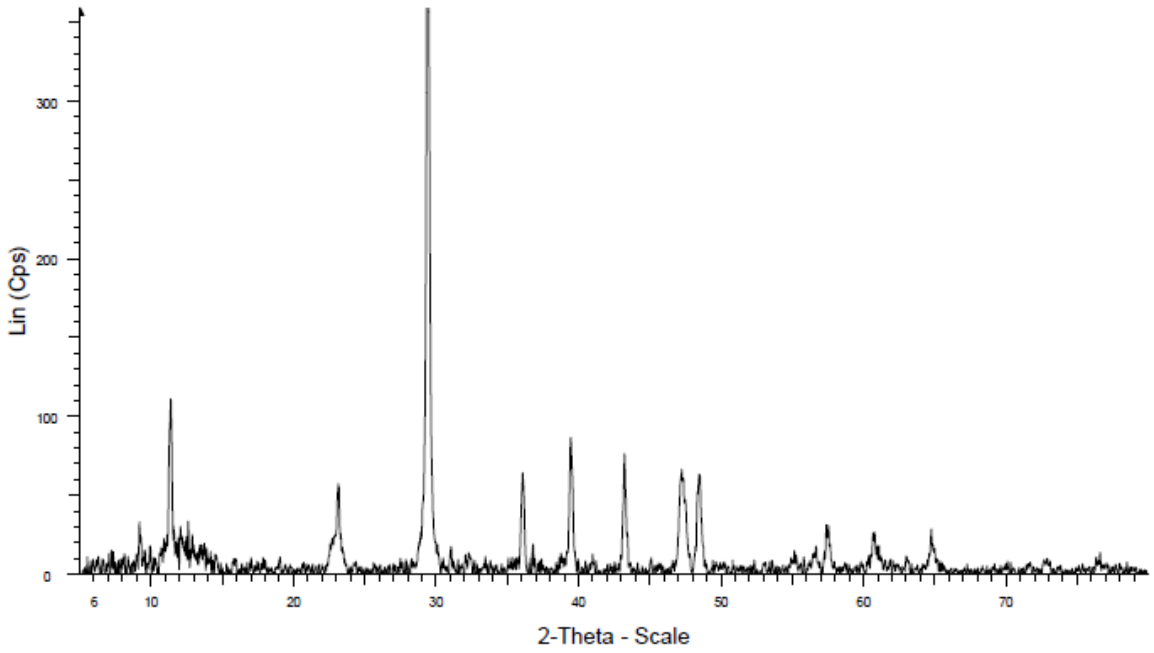

Figure D. 19 X-Ray Diffractogram Obtained for WW50T7D

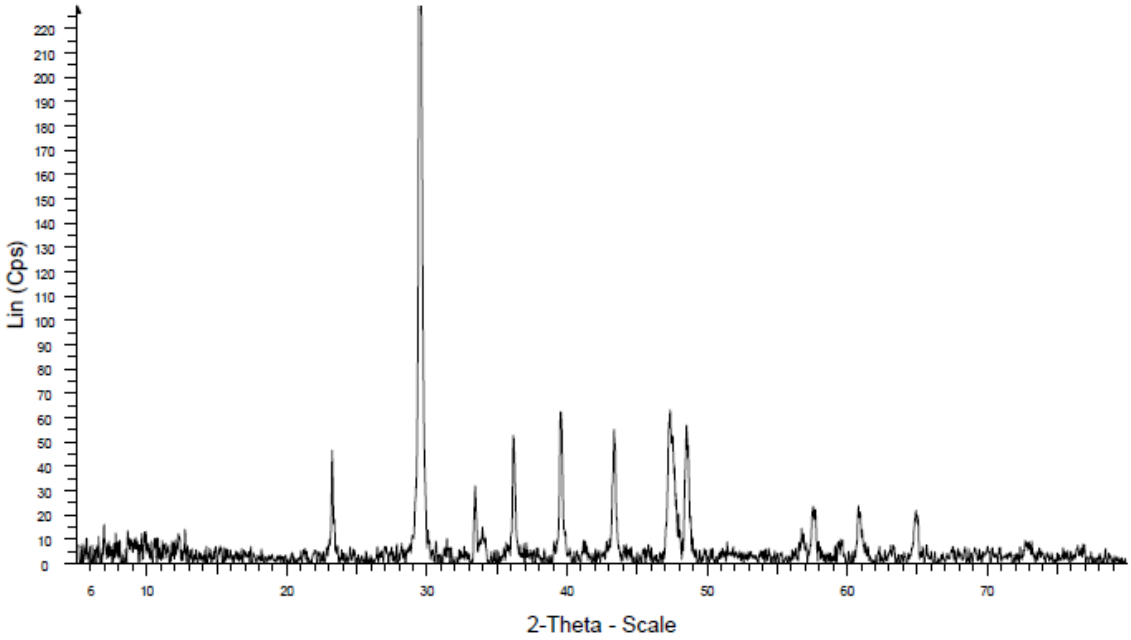

Figure D. 20 X-Ray Diffractogram Obtained for WW75T0H

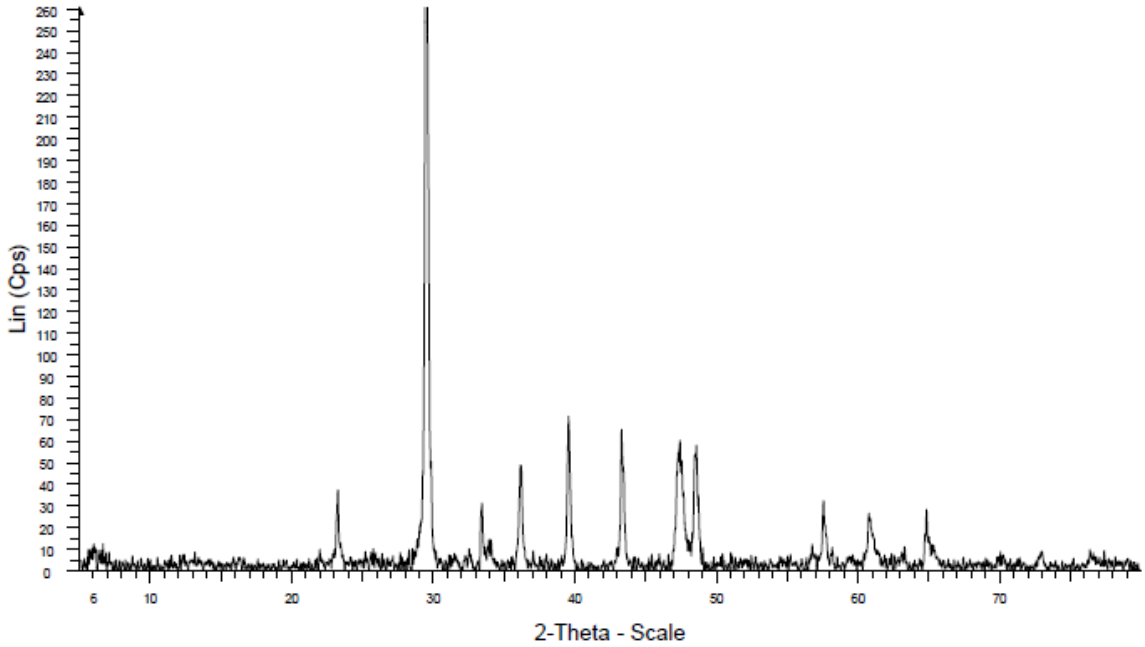

Figure D. 21 X-Ray Diffractogram Obtained for WW75T1H

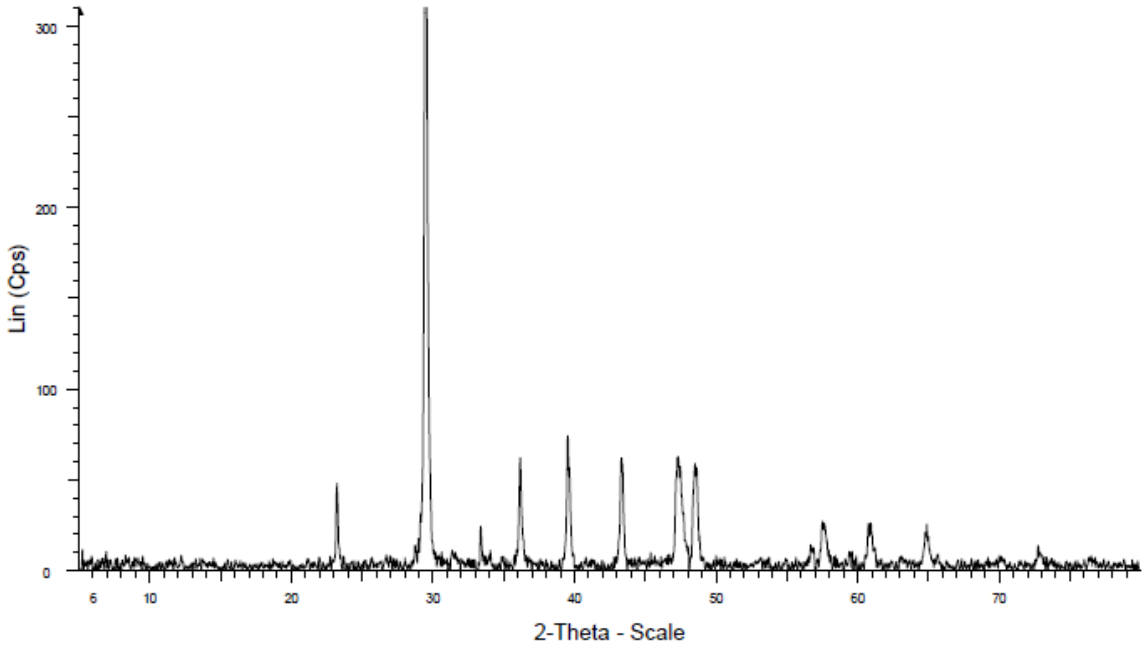

Figure D. 22 X-Ray Diffractogram Obtained for WW75T3H

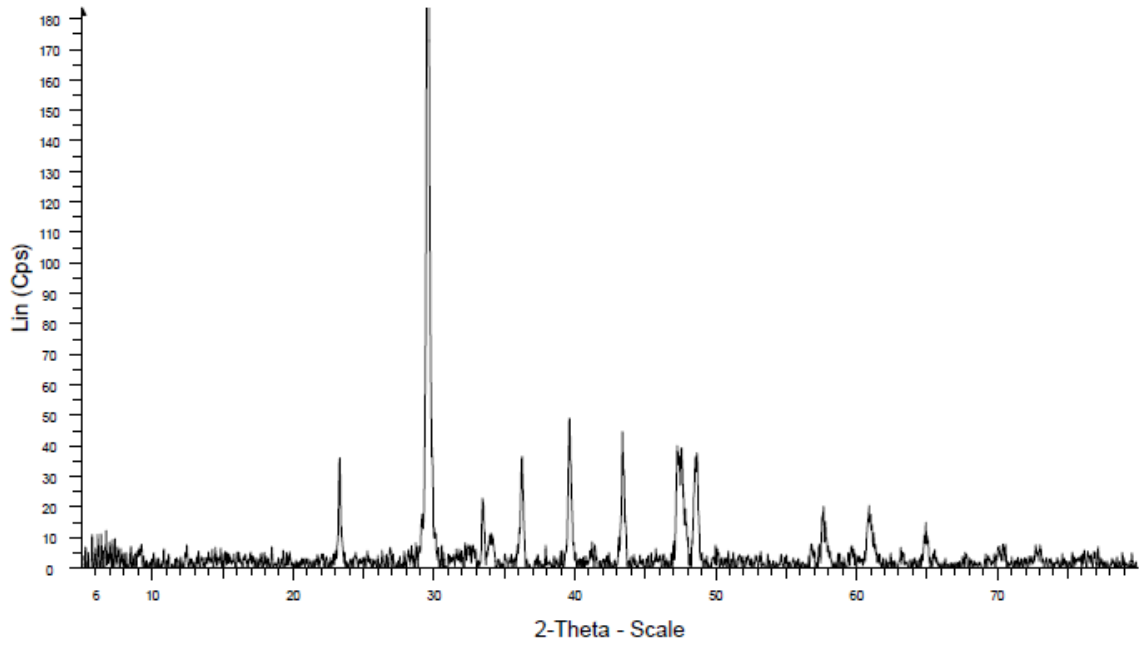

Figure D. 23 X-Ray Diffractogram Obtained for WW75T1D

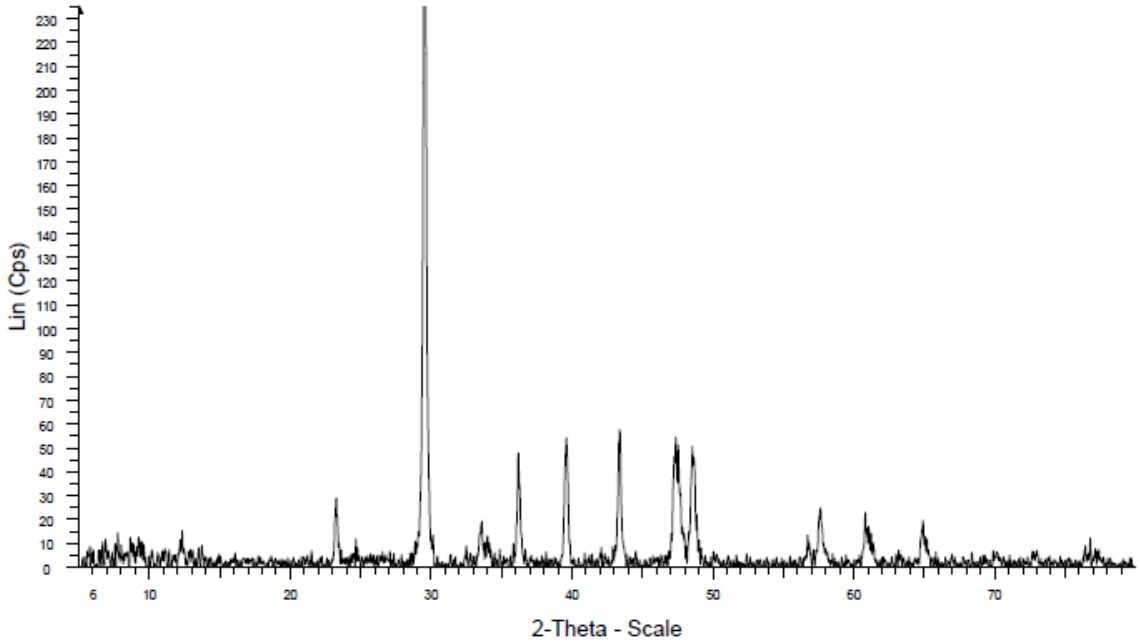

Figure D. 24 X-Ray Diffractogram Obtained for WW75T3D

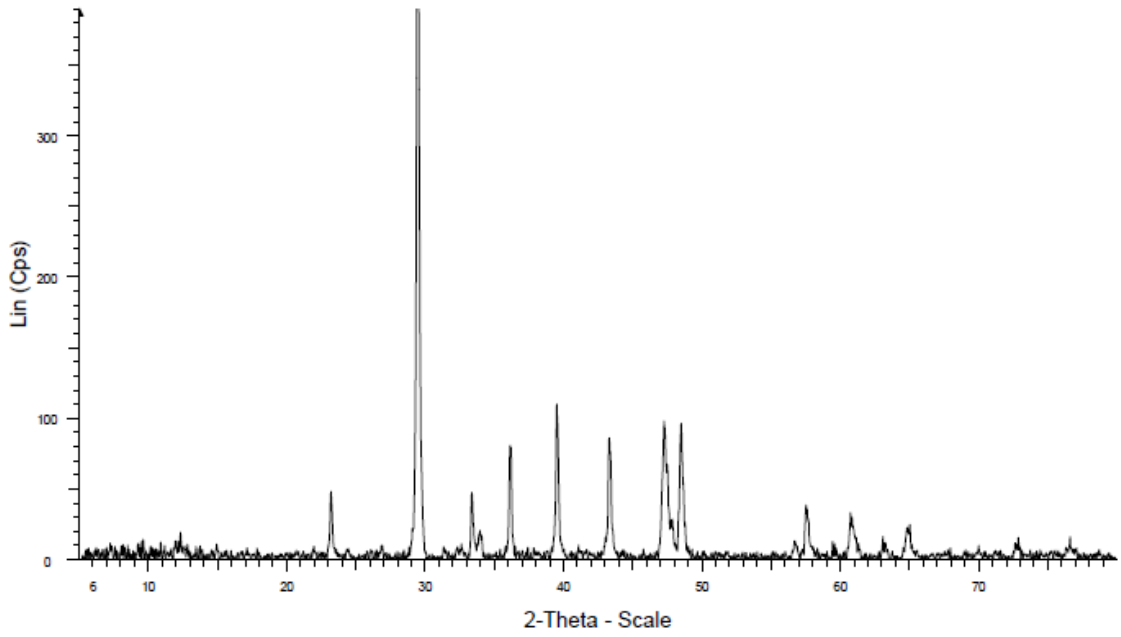

Figure D. 25 X-Ray Diffractogram Obtained for WW75T7D

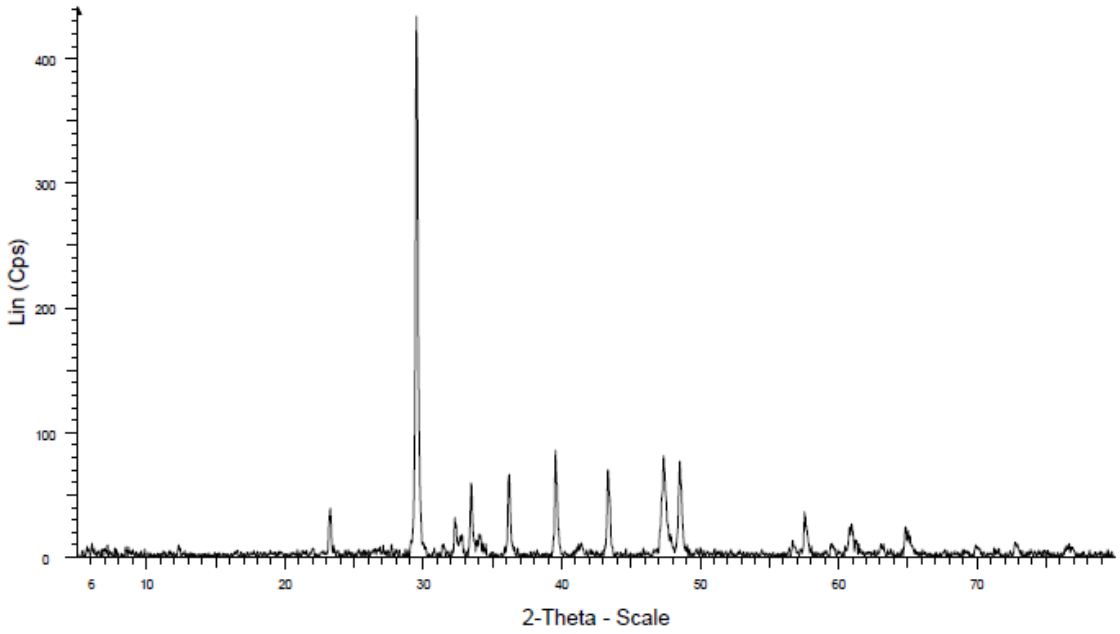

Figure D. 26 X-Ray Diffractogram Obtained for WWT0H

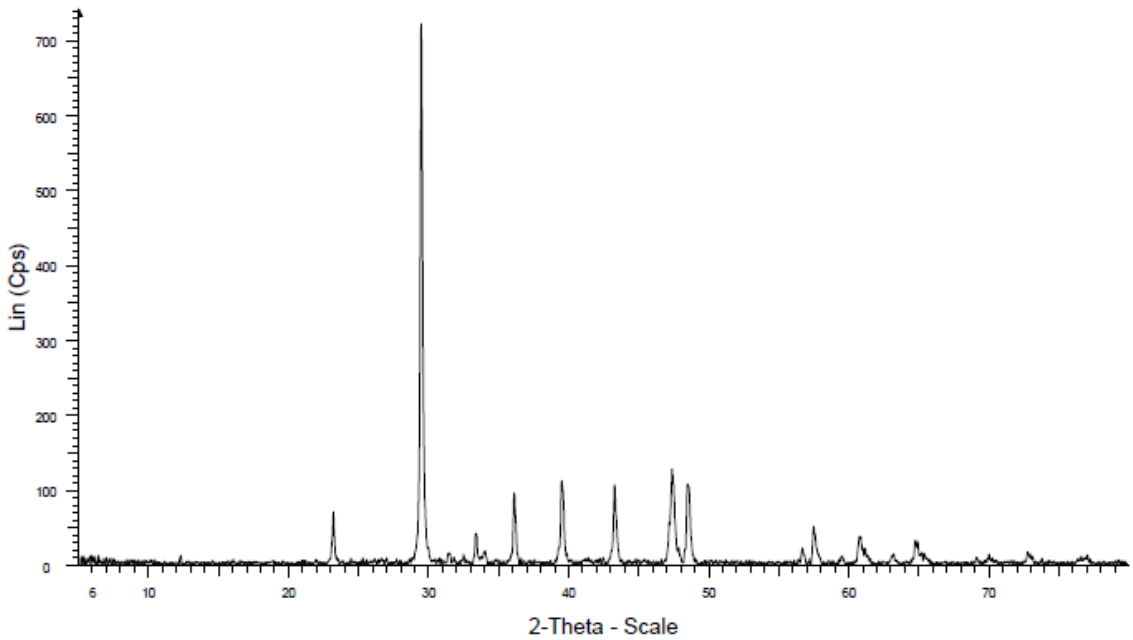

Figure D. 27 X-Ray Diffractogram Obtained for WWT1H

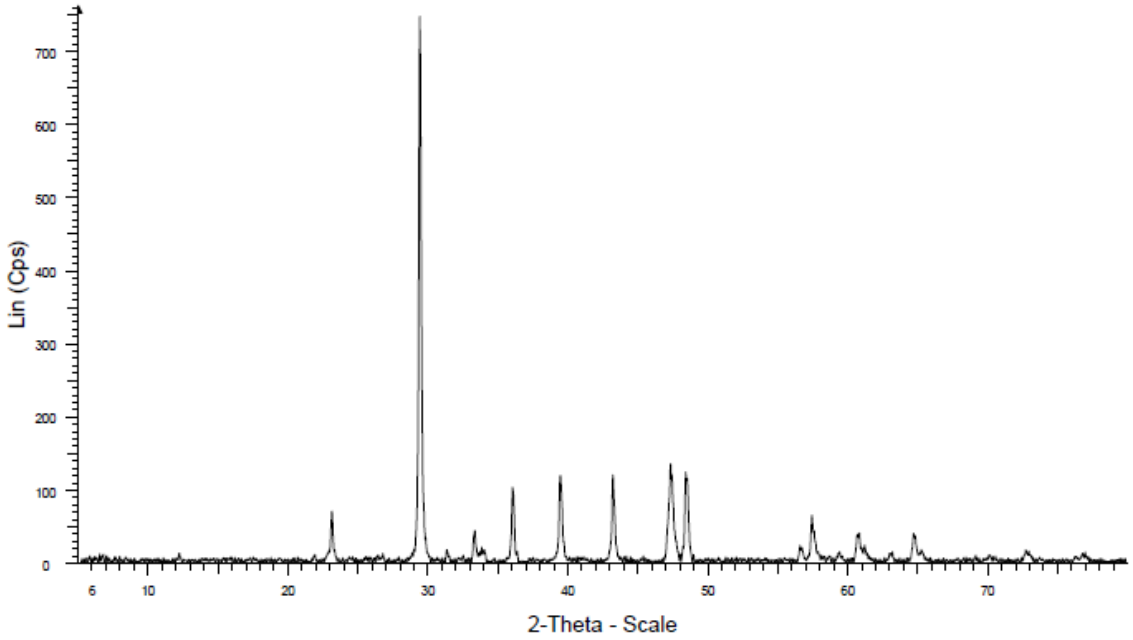

Figure D. 28 X-Ray Diffractogram Obtained for WWT3H

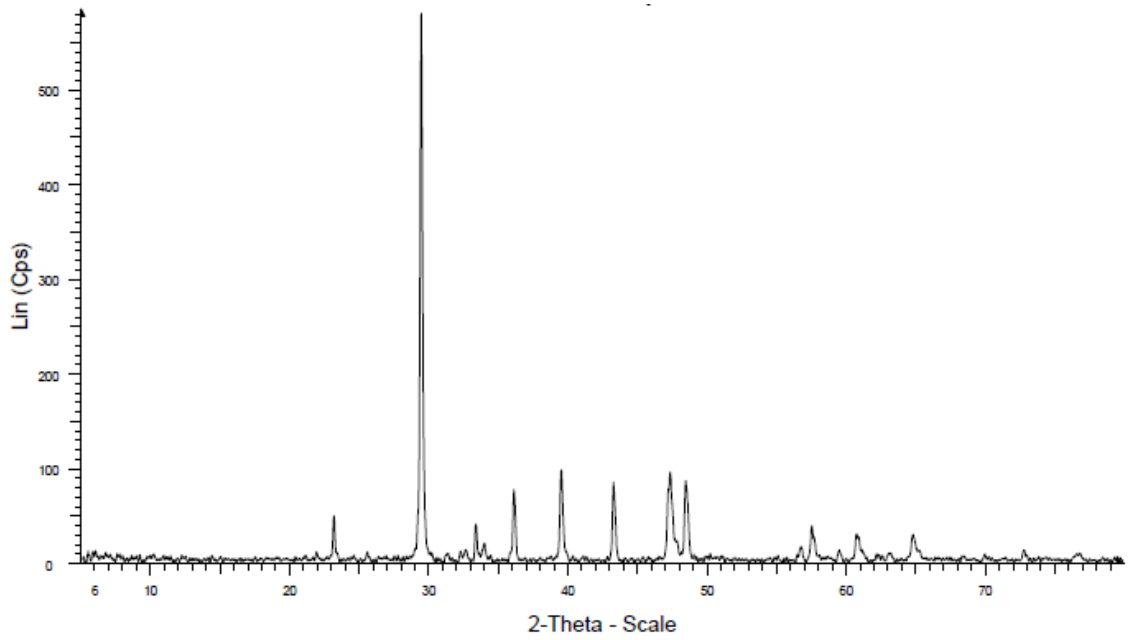

Figure D. 29 X-Ray Diffractogram Obtained for WWT1D

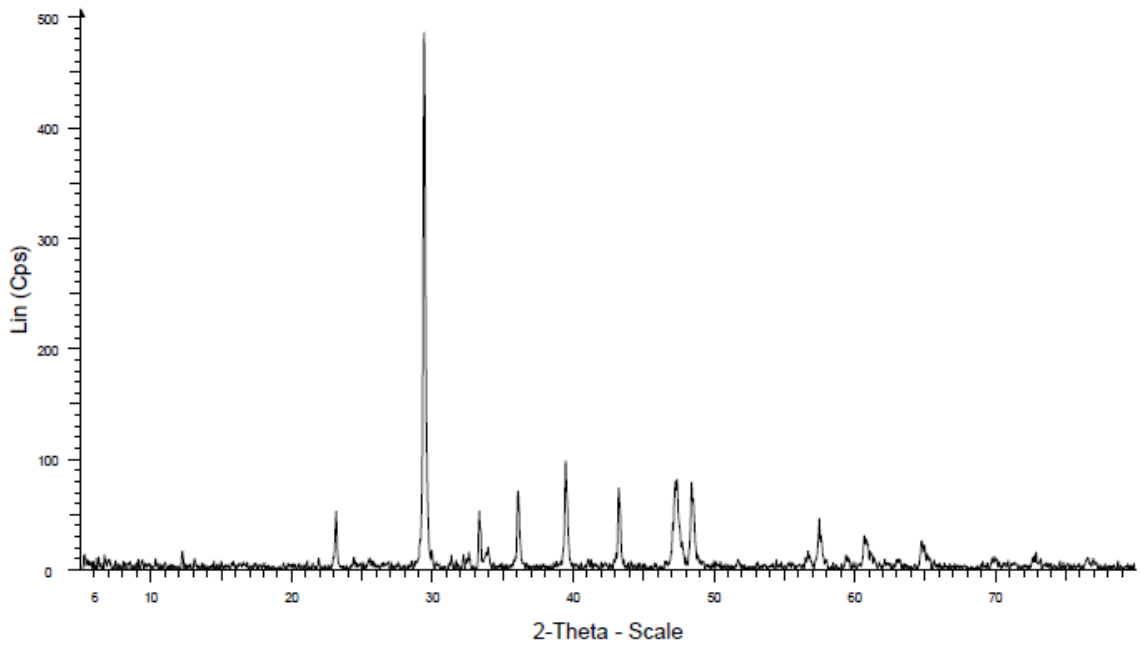

Figure D. 30 X-Ray Diffractogram Obtained for WWT3D

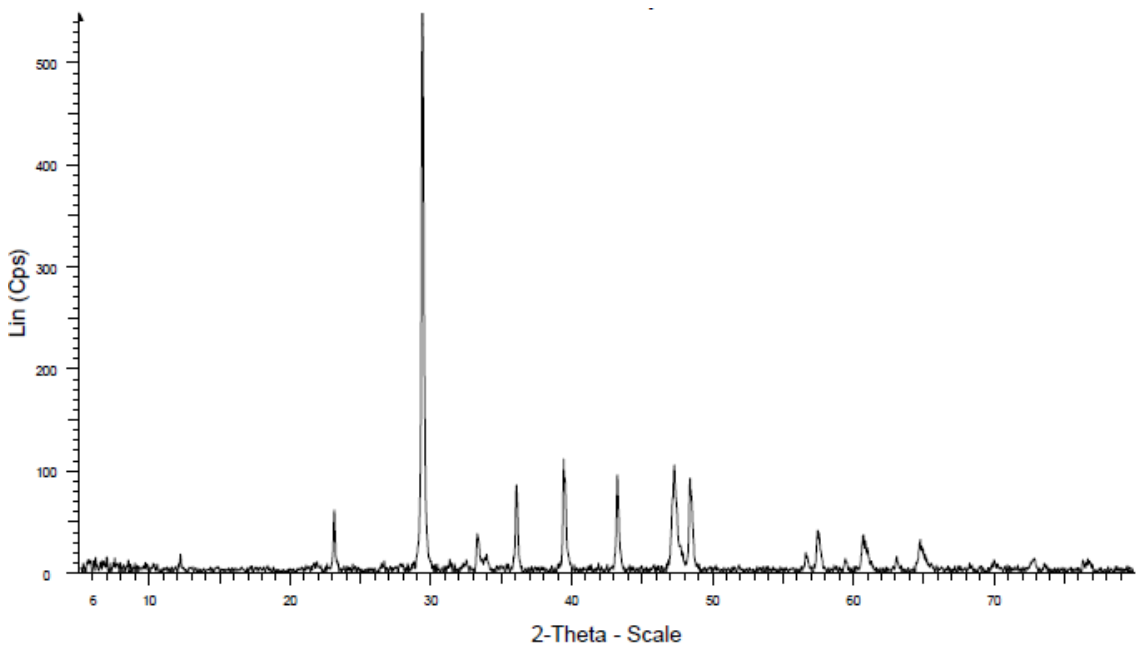

Figure D. 31 X-Ray Diffractogram Obtained for WWT7D

Appendix E

Wash Water Test Data

Table E. 1 Thermogravimetric Analysis Data

CO_2 (%)	Sample ID	CBW (%)	CH (%)
0	0H	3.22	3.35
	1H	3.92	3.77
	3H	3.50	3.50
	1D	8.17	4.54
	3D	9.35	5.30
	7D	9.61	5.85
25	0H	3.18	2.97
	1H	4.59	3.55
	3H	4.91	3.53
	1D	5.91	3.86
	3D	7.78	4.33
	7D	7.56	3.60
50	0H	3.05	2.57
	1H	3.50	2.33
	3H	3.61	2.84
	1D	4.43	3.13
	3D	5.16	3.27
	7D	5.39	3.21
75	0H	3.04	2.45
	1H	3.08	2.55
	3H	3.17	2.77
	1D	3.28	2.92
	3D	2.89	3.11
	7D	3.16	3.04
100	0H	3.02	2.35
	1H	3.01	2.26
	3H	3.04	2.49
	1D	2.84	2.70
	3D	2.84	2.87
	7D	2.76	2.87

Table E. 2 The Concentration of Anions in Wash Water

Sample ID	Age (hours)	pH	Anions (ppm)	
			Cl^-	SO_4^{2-}
WWU	0	13.02	32.75	26.50
WWT0H	0	7.01	29.64	1611.99
WWT1H	1	8.35	33.25	1404.11
WWT3H	3	9.91	33.00	1488.34
WWT1D	24	10.26	30.54	1797.49
WWT3D	72	10.54	30.68	1839.70
WWT7D	168	10.67	30.63	1936.70

Table E. 3 The Concentration of Cations in Wash Water

Sample ID	Age (hours)	Cations (ppm)					Alkali [Na_2O eq] (ppm)
		Na^+	K^+	Ca^{2+}	Al^{3+}	Si^{4+}	
WWU	0	63.09	738.73	708.09	< 3.0	230.64	670.58
WWT0H	0	27.12	667.40	301.48	< 3.0	82.81	565.56
WWT1H	1	24.82	689.34	240.95	< 3.0	59.59	579.84
WWT3H	3	29.11	668.95	323.15	< 3.0	60.60	569.47
WWT1D	24	23.17	718.40	453.93	< 3.0	57.19	600.66
WWT3D	72	23.04	717.50	465.67	< 3.0	52.61	599.76
WWT7D	168	23.16	753.98	499.78	< 3.0	49.17	628.85

Appendix F

Mortar Test Data

Table F. 1 Compressive Strength Data for Mortar Mixtures

Sample ID	Compressive Strength (MPa)		
	1-day	7-day	28-day
W/C Ratio - 0.485			
CTRL	16.5	37.2	42.6
WWU	17.8	42.7	49.5
WWUC	15.2	38.4	47.6
WWT	16.0	41.6	51.1
WWTC	9.1	33.4	40.3
WWT50	15.8	40.2	49.4
WWT50C	12.1	35.2	45.4
WW50T	15.4	41.9	51.0
WW50TC	11.5	35.3	45.3
W/C Ratio - 0.42			
CTRL-42	26.9	46.3	50.2
WWT-42	21.7	47.4	55.5
WWTC-42	16.7	39.0	47.2
W/C Ratio - 0.55			
CTRL-55	15.8	35.5	40.6
WWT-55	16.4	37.9	46.4
WWTC-55	10.6	30.3	36.4

Appendix G

Concrete Test Data

Table G. 1 Combined Test Data for Concrete Mixtures

Test	CTRL	WWU50	WWU	WWT50	WWT	WWTC	WW50T
CStr-1d	28.7	27.3	30.3	28.3	28.0	19.7	25.3
CStr-3d	31.7	32.7	34.0	32.7	32.3	26.7	29.0
CStr-7d	37.0	34.7	37.3	37.7	36.7	32.3	34.7
CStr-28d	42.0	42.7	43.3	43.3	42.7	38.7	43.7
CStr-91d	45.3	45.3	48.0	48.0	48.3	44.3	47.7
BRes-28d	5.46	5.31	5.89	5.87	5.99	5.21	5.80
BRes-91d	7.94	7.98	8.35	8.20	8.19	7.59	8.03
SRes-28d	11.03	10.93	12.57	12.03	11.93	10.70	11.77
SRes-91d	14.27	14.77	15.73	15.53	15.37	13.57	15.27
STen-28d	4.97	4.91	4.91	4.96	4.93	4.56	4.87
MoR-28d	7.15	7.16	7.01	7.23	7.00	6.22	7.26
FT-300c	95	94	96	96	94	92	93

Curriculum Vitae

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2018-2020	M.Sc.E.	University of New Brunswick
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Banujan, B., Nayanthara, PGN., Chamikara, CSS., and Rohitha, LPS. 2016. Plant Design for Upgrading Disseminated Graphite to 97-99% Carbon Grade. *In* Proceedings of the ASEAN++2016: 12th International Conference on Mining, Material and Petroleum Engineering. Thailand, 28-29 July 2016. Chulalongkorn University, Bangkok, Thailand.

Nayanthara, PGN., Banujan, B., Chamikara, CSS., and Rohitha, LPS. 2016. Froth Flotation Cell Design to Upgrade Graphite for Mineral Processing Industry. *In* Proceedings of the ASEAN++2016: 12th International Conference on Mining, Material and Petroleum Engineering, Thailand, 28-29 July 2016. Chulalongkorn University, Bangkok, Thailand.

Conference Presentations:

Banujan, B., Pathirana,GPDH., Ranaweera, DKL. 2016. Identification of the Most Suitable Location in Kaduwela Area to Establish a Mega Quarry Site to Supply Aggregate Requirements of Mega Projects in Colombo. ERE 2016 Annual Conference, Colombo. University of Moratuwa, Sri Lanka.