PRODUCTION AND CHARACTERIZATION OF ECO-CEMENT FROM MUNICIPAL SOLID WASTE INCINERATION RESIDUES

By

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ABSTRACT

This research program was aimed at developing cement ecologically from municipal solid waste incineration (MSWI) residues utilizing the wastes, reducing carbon emission and minimizing the natural resource consumption. Two types of eco-cements were produced; one with 100% MSWI residues and the other with 94% MSWI residues and 6% additives, with a clinkering temperature of 1100°C. The eco-cement demonstrated non-hydraulic behavior; however, it could be consolidated upon carbonation activation, forming a binding matrix comprised of amorphous calcium silicate hydrocarbonate, $CaCO_3$, and gypsum. Carbonation activation of eco-cement for two hours showed compressive strength comparable to the 28 days strength of ordinary Portland cement upon hydration. Carbonation up to twelve hours further improved the compressive strength by 50% in comparison to the two hours results. Microstructural studies confirmed chloroellestadite (CE) and belite as the main strength contributors along with CO_2 reactive phases in the eco-cement. For a better understanding of the carbonation reactivity and strength contribution of these phases, both chloroellestadite and belite were synthesized. Carbonation cured synthesized CE and belite showed strength behavior similar to that of eco-cement, and the carbonation-derived phases of synthesized compounds confirmed the development of $CaCO_3$, gypsum, and calcium silicate hydrocarbonate as a strength contributing matrix. Eco-concrete slabs were produced to assess the binding properties of the eco-cement with compressive strength comparable to that of OPC concrete. Finally, extensive environmental testing results showed that the clinkering and carbonation curing process helped immobilize the hazardous elements such as heavy metals, organic compounds and dioxin, and furans. These results show that eco-cement can be safely used in commercial applications.

RÉSUMÉ

Ce travail de recherche a démontré que le ciment peut être fabriqué écologiquement à partir de résidus municipaux d'incinération des déchets solides pour réduire l'émission de carbone, utiliser les déchets et minimiser la consommation de ressources naturelles. Deux types d'éco-ciments ont été produits; un avec des résidus de 100% de MSWI et un avec 94% de résidus de MSWI et 6% d'additifs, avec une température de clintage de 1100 °C. L'éco-ciment a montré un comportement non-hydraulique mais pourrait être consolidé lors de l'activation de la carbonatation, formant une matrice de liaison composée d'hydrocarbonate de silicate de calcium amorphe, de $CaCO_3$ et de gypse. L'activation de la carbonatation de l'éco-ciment par deux heures a montré une résistance à la compression comparable à la résistance d'hydratation de 28 jours du ciment Portland ordinaire. La carbonatation jusqu'à douze heures a encore amélioré la résistance à la compression de 50% par rapport aux résultats de deux heures. Les études microstructurales confèrent au chloroellestadite et au bélite le principal facteur de force et les phases de réaction au CO_2 dans l'éco-ciment. Pour une meilleure compréhension de la réactivité de la carbonatation et la contribution de la force de ces phases, le chloroellestadite et le bélite ont été synthétisés. La carbonatation polymérisée ce et le bélite ont montré des analogues de comportement de résistance à l'éco-ciment, et les phases dérivées de carbonatation des composés synthétisés ont confirmé le développement du $CaCO_3$, du gypse et de l'Hydrocarbonat de silicate de calcium comme force matrice contributif. Des dalles d'éco-béton ont été produites pour évaluer les propriétés de liaison de l'éco-ciment avec une résistance à la compression comparable au béton

OPC. Enfin, de vastes résultats de tests environnementaux ont montré que le processus de polymérisation et de carbonatation a permis d'immobiliser l'élément dangereux tel que les métaux lourds, les composés organiques et les dioxines et les furannes. Ces résultats ont montré que l'éco-ciment peut être utilisé en toute sécurité dans les applications commerciales.

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STATEMENT OF ORIGINALITY

- Eco-cement was produced entirely from MSWI residues; compacts of eco-cement can demonstrate a compressive strength of 60MPa after 28 days of subsequent hydration followed by two hours of carbonation activation. This is the highest strength ever reported in the literature for an MSWI derived cement binder.
- Eco-cement derived from 94 % MSWI residues compacts can gain a compressive strength of 55 MPa in just two hours of carbonation activation, analogous to the 28 days hydration strength of OPC. This is the highest strength reported in the literature for eco-cement produced by using all types of MSWI residues i.e. bottom ash, boiler ash, and air pollution control (APC) residues.
- Different microstructural investigating techniques were successfully used to resolve the nanostructure of the carbonation activated eco-cement. The carbonation- derived matrix was composed of $CaCO_3$, gypsum and amorphous calcium silicate carbo-hydrate.
- The carbonation reactivity, strength development, and microstructure of the synthesized CE were studied in detail and reported for the first time. Studies revealed that the CE showed non-hydraulic behavior; however, it can hold very high CO_2 reactivity. Synthesized CE showed around 28 MPa compressive strength after carbonation curing of twelve hours. The resultant matrix was comprised of gypsum, $CaCO_3$, and amorphous calcium silicate hydrocarbonate.

PUBLICATIONS

Muhammad Shoaib Ashraf and Yixin Shao. *Production of Eco-Cement using MSW Incineration Energy and Residues*, paper ready to be submitted, target journal: Resources, Conservation and Recycling

This paper is based on Chapter 3.

Muhammad Shoaib Ashraf and Yixin Shao. *Characterization of Eco-Cement made from Municipal Solid Waste Incineration Residues,* paper ready to be submitted, target journal: Cement and Concrete Research

This paper is based on Chapter 4.

Muhammad Shoaib Ashraf andYixin Shao. *Synthesis and Characterization of Chlorellestadite and Belite to Simulate Eco-cement made from Municipal Solid Waste Incineration Residues*, paper ready to be submitted, target journal: Cement and Concrete Research

This paper is based on Chapter 5

Muhammad Shoaib Ashraf and Yixin Shao. *Environmental Impact Assessment of Eco-Cement made from Municipal Solid Waste Incineration Residues, paper* ready to be submitted, target journal: International Journal of Integrated Waste Management, Science and Technology

This paper is based on Chapter 6

CONTRIBUTION OF THE AUTHOR

The manuscripts included in this thesis (Chapters 3 to 6) will be submitted for publication in scientific journals. The author was responsible for conducting the research, analyzing the data, and preparing the manuscripts. The author's supervisor, Prof. Yixin Shao, provided general guidance and editorial revisions throughout the entire process.

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CHAPTER 1. INTRODUCTION

1.1. OVERVIEW

The production of municipal solid wastes (MSW) is estimated to be about 1 to 2 billion tons per year worldwide [1]. Normally, MSW is either landfilled or incinerated. Compared to the landfill, incineration reduces the volume of the waste and produces energy during the incineration process because the MSW has high calorific values. In areas where the population densities are moderately high, and the landfill sites are limited, the incineration of MSW is the desirable choice [2]. However, incineration is still not popular. In Canada, only 5% of MSW is processed by incineration. A vast majority is disposed of in a landfill. This is because the incineration of MSW results in large quantities of ash residues, including the bottom ash, fly ash and air pollution control (APC) lime residues. Although the bottom ashes are not considered to be hazardous materials, fly ash or APC residues require special sites for disposal. The bottom ashes are produced at a rate of about 250–300 kg/1000 kg of waste) and fly ash or APC residues at about 25–30 kg/1000 kg of wastes [3].

Recycling and reusing are the best strategies for the management of municipal solid waste incineration (MSWI) residues. The major elements of these MSWI residues are Ca, Si, Al, Fe, Mg, Cl, Na and K, and the common oxides found in these residues are CaO, SiO_2, Na_2O, K_2O, Al_2O_3, and SiO_2. These SMWI residues are utilized in different ways in different countries [4-8]. The bottom ashes are commonly used in roads as a base material in concrete and asphalt pavements [9]. Furthermore, numerous researchers effectively used the MSW incineration (MSWI) residues to produce environmentally friendly cement. Cement produced by using 15 % of MSWI residues as a raw meal and sintered at 1400°C demonstrated very low compressive strength of 7 MPa [10]. Shi et al. produced sulphoaluminate cement by using 30% MSWI fly ash as a raw feed of cement clinkers, the clinkering was carried out at 1300°C and a 28-days cement paste compressive strength of 80 MPa was reported [11]. Production of cement using 50% MSWI ash was demonstrated on a pilot scale (50 ton/day), with the clinkering process being conducted in a rotary kiln at a temperature of 1400°C. The compressive strength of 35 MPa was attained after 28-days of moist curing [12]. The term “eco-cement” was firstly used by Shimoda and Yokoyama (1999), up to 50 % MSWI residues were used as a raw meal of cement clinker. Eco-cement was produced at 1350 °C, and it showed hydraulic reactivity identical to that of OPC. The compressive strength of 53 MPa was reported after 28-days curing time [13]. The cement produced using MSWI residues showed hydraulic properties because those cements were produced at an elevated temperature in the ranges from 1350°C to 1400°C. Recently, Zaid and Shao have successfully produced a carbonation activated cement binder by using a mixture proportion containing 85 % of MSWI residues at a clinkering temperature as low as 1000 °C. The cement binder showed no hydraulic reactivity, but it achieved a compressive strength over 50 MPa with a carbon dioxide uptake capacity of about 7% [14].

Production of cement is very energy intensive and its production requires vast quantities of a natural resource, i.e., each ton of cement production requires more than 1.6 ton of natural resources, which are limited on planet earth. Burning of the fossil fuels to fulfill the energy required to produce cement and calcination of limestone emits a very high amount of CO_2; a ton of CO_2 is emitted during the production of each ton of cement. This is why the cement industry is the largest source of CO_2 emitter. Cement industry emits about 5 % of the total CO_2 emissions worldwide [15, 16]. Accordingly, one of the major challenges for the concrete and cement industry is to find an alternative binding cementitious system with low carbon emissions as compared to the OPC. Belite-based cement is a classic example and is considered more sustainable as compared to the OPC because these types of cement are produced at a lower temperature and emit a lesser amount of CO_2. Due to the lack of hydraulic reactivity of belite, it has been considered as undesirable components of OPC. Conversely, the belite was found to exhibit enhanced reactivity in the presence of CO_2. When subjected to carbonation curing, these binder systems can store CO_2 (up to 17 % in the case of calcium silicate cements [17]. Production of these cement binders at lower temperatures, along with the CO_2 storage capacity results in a reduction of the overall carbon footprint of concrete as compared with the OPC concrete. The carbon footprint of carbonated calcium silicate cement concrete has been reported to be about 70% of OPC concrete [18].

Carbonation activation is defined as a chemical reaction between CO_2 and tri-calcium silicate ($3CaO{\cdot}SiO_2$ or C3S) and/or dicalcium silicate ($2CaO{\cdot}SiO_2$ or C2S) in the cement paste. Immediately after casting, CO2 is deliberately introduced to fresh cement paste. The hybrids of calcium silicate hydrate (3CaO·2SiO2·3H2O or CSH) and calcium carbonate ($CaCO_3$) are produced as the result of the carbonation process [19] given by Equations 1.1 and 1.2.

$$2(3CaO{\cdot}SiO_2) + 3CO_2 + 3H2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + 3CaCO_3 \quad (1.1)$$

$$2(2CaO{\cdot}SiO_2) + CO_2 + 3H2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + CaCO_3 \quad (1.2)$$

Due to depletion of calcium hydroxide ($Ca(OH)_2$), the carbonated concrete products can perform better in term of durability, strength, dimensional stability, as compared with the regular OPC concrete. The best application of early age carbonated concrete is the manufacturing of concrete bricks/blocks and unreinforced precast concrete products. The carbonation curing of fresh concrete is different from weathering carbonation of mature concrete. The carbonation of hardened concrete during its service life converts C-S-H to silica gel, which results in the loss of strength in concrete, leading to durability problems [20-22].

In addition to the valuable minerals and oxides, these MSWI residues also contain heavy metals, dioxin, and organic compounds. MSWI residues contain Cr, Cu, Hg, Cd, Zn, Ni, and Pb, where usually Pb and Zn exist in large quantities. Leaching of heavy metals can be reduced by early age carbonation treatment of cement produced using MSWI ashes. The volume expansion is associated with the formation of CaCO3, which helps in the reduction of the porosity and in the withholding of heavy metals [23]. The mobility of certain heavy metals, such as Pb, Zn, Cu, Cd, and Cr can be reduced, or regulated by the neutralization of pH which is caused by the formation of carbonate minerals due to carbonation [24, 25]. Carbonation is quite often used in waste treatment to reduce leaching of heavy metals before landfill [26]. Additionally, the past research showed that the high-temperature clinkering could bind these chlorides into a stable structure, followed by the hydration process which further reduces the amount of soluble chlorides due to retention within the hydrated products [27].

1.2. RESEARCH OBJECTIVES

This proposed research program was sought to develop an eco-cement from MSWI residues and carbon dioxide. The following tasks were carried out to develop eco-cement:

- To make eco-cement from MSWI residues. The target was to make eco-cement with 90-100% wastes. The mechanical performance should be comparable to that of OPC.
- To derive the eco-cement at lower clinkering temperature around 1000°C to 1100 °C, so that in the future eco-cement can be produced in an incinerator, rather than in a cement kiln at a cement plant. In this case, an incinerator can be turned into an environment-friendly cement production facility. Incineration energy can be innovatively utilized for eco-cement clinkering which consumes no fossil fuels.
- To maximize carbonation curing for strength activation and carbon sequestration in the eco-cement products.
- To optimize the production line of eco-cement to maximize performance and energy efficiency, and to minimize the production time and cost.
- To investigate the phases produced during clinkering and the phases developed after the carbonation curing of eco-cement.
- To synthesize the CO_2 reactive phases of eco-cement for the better understanding of strength development mechanism.
- To perform the environmental assessment of eco-cement derived from MSWI residues in terms of hazardous materials such as heavy metals, organic compounds, and dioxin.

1.3. THESIS STRUCTURE

This thesis follows manuscript-based structure. Each chapter has followed a preface which highlighted its objectives and the relationship to other chapters. A brief literature review of the past research is included on each specific topic to highlight the contribution of each chapter.

Chapter 1 includes the background, the significance and the objective of the proposed research.

Chapter 2 summarize the previous research related to MSWI residues and their uses, eco-cement, and carbonation.

Chapter 3 describes the production of eco-cement using MSW incineration energy and residues. This chapter describes a manufacturing approach to produce eco-cement from MSWI residues based on extensive parametric studies. The basic process included proportioning – blending-clinkering- and carbonation and was optimized. To serve the purpose, different proportions of MSWI residues to maximize their usage in the eco-cement, blending techniques to find optimum mixing; the and effects of clinker size and clinkering temperatures were also discussed.

Chapter 4 presents the characterization of eco-cement made from MSW incineration residues. It provides a detailed characterization of the eco-cement phases after the clinkering and phases developed after the carbonation activation. Techniques including quantitative X-ray diffraction (QXRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and Fourier-transform infrared (FTIR) spectroscopy were used for microstructural studies.

Chapter 5 provides the details of the synthesis and characterization of chlorellestadite and belite to simulate eco-cement made from MSW incineration residues. This chapter also summarizes details of the production and characterization of synthesized phases. Chlorellestadite (CE) and belite were synthesized, and the carbonation reactivity was studied using different microstructural investigating techniques such as QXRD, TGA, TEM, and SEM. This chapter is aimed at understanding the strength mechanism of the brand-new eco-cement.

Chapter 6 reviews the environmental impact assessment of eco-cement made from municipal solid waste incineration residues. It explains the environmental assessment of eco-cement. Effect of clinkering and carbonation on the hazardous elements is examined and discussed in chapter 6. A brief review of the impact of heavy metals, organic compounds, and dioxin is undertaken in Chapter 6.

Conclusions are summarized in Chapter 7, along with the suggestions of future work.

REFERENCES

1. Hoornweg, D. and P. Bhada-Tata, *What a waste: a global review of solid waste management.* What A Waste: A Global Review of Solid Waste Management, 2012.
2. Stehlík, P., *Contribution to advances in waste-to-energy technologies.* Journal of Cleaner Production, 2009. **17**(10): p. 919-931.
3. Aubert, J.E., B. Husson, and A. Vaquier, *Use of municipal solid waste incineration fly ash in concrete.* Cement and Concrete Research, 2004. **34**(6): p. 957-963.
4. Sawell, S.E., A.J. Chandler, T.T. Eighmy, J. Hartlén, O. Hjelmar, D. Kosson, H.A. Van Der Sloot, and J. Vehlow, *An international perspective on the characterisation and management of residues from MSW incinerators.* Biomass and Bioenergy, 1995. **9**(1-5): p. 377-386.
5. Skodras, G., P. Grammelis, E. Kakaras, D. Karangelos, M. Anagnostakis, and E. Hinis, *Quality characteristics of Greek fly ashes and potential uses.* Fuel Processing Technology, 2007. **88**(1): p. 77-85.
6. Lam, C.H.K., A.W.M. Ip, J.P. Barford, and G. McKay, *Use of Incineration MSW Ash: A Review.* Sustainability, 2010. **2**(7).
7. Hjelmar, O., *Waste management in Denmark.* Waste Management, 1996. **16**(5-6): p. 389-394.
8. Sakai, S., S.E. Sawell, A.J. Chandler, T.T. Eighmy, D.S. Kosson, J. Vehlow, H.A. Van Der Sloot, J. Hartlén, and O. Hjelmar, *World trends in municipal solid waste management.* Waste Management, 1996. **16**(5-6): p. 341-350.
9. Wiles, C.C., *Municipal solid waste combustion ash: State-of-the-knowledge.* Journal of Hazardous Materials, 1996. **47**(1): p. 325-344.
10. Shih, P.H., J.E. Chang, and L.C. Chiang, *Replacement of raw mix in cement production by municipal solid waste incineration ash.* Cement and Concrete Research, 2003. **33**(11): p. 1831-1836.
11. Shi, H.s., K. Deng, F. Yuan, and K. Wu, *Preparation of the saving-energy sulphoaluminate cement using MSWI fly ash.* Journal of Hazardous Materials, 2009. **169**(1-3): p. 551-555.
12. Kikuchi, R., *Recycling of municipal solid waste for cement production: Pilot-scale test for transforming incineration ash of solid waste into cement clinker.* Resources, Conservation and Recycling, 2001. **31**(2): p. 137-147.
13. Shimoda, T. and S. Yokoyama. *Eco-cement: A new Portland cement to solve municipal and industrial waste problems*. in *Proceedings of the International Conference held at the University of Dundee, Dundee September*. 1999.
14. Ghouleh, Z. and Y. Shao, *Turning municipal solid waste incineration into a cleaner cement production.* Journal of Cleaner Production, 2018. **195**: p. 268-279.
15. Scalenghe, R., F. Malucelli, F. Ungaro, L. Perazzone, N. Filippi, and A.C. Edwards, *Influence of 150 years of land use on anthropogenic and natural carbon stocks in emilia-*

romagna region (Italy). Environmental Science and Technology, 2011. **45**(12): p. 5112-5117.

16. Humphreys, K. and M. Mahasenan, *Toward a Sustainable Cement Industry, Substudy 8, World Business Council for Sustainable Development, Report.* 2002.
17. Ashraf, W., J. Olek, and V. Atakan. *Carbonation reaction kinetics, CO2 sequestration capacity, and microstructure of hydraulic and non-hydraulic cementitious binders*. in *Sustainable Construction Materials and Technologies*. 2016.
18. Sahu, S. and N. DeCristofaro, *Solidia Cement™, Solidia Technologies. White Paper.* 2013.
19. Young, J.F., R.L. Berger, and J. Breese, *Accelerated Curing of Compacted Calcium Silicate Mortars on Exposure to CO2.* Journal of the American Ceramic Society, 1974. **57**(9): p. 394-397.
20. Feng, B., D.M. Cao, W.J. Meng, J. Xu, R.C. Tittsworth, L.E. Rehn, P.M. Baldo, and G.L. Doll, *Characterization of microstructure and mechanical behavior of sputter deposited Ti-containing amorphous carbon coatings.* Surface and Coatings Technology, 2001. **148**(2): p. 153-162.
21. Pellenq, R.J.M., N. Lequeux, and H. van Damme, *Engineering the bonding scheme in C-S-H: The iono-covalent framework.* Cement and Concrete Research, 2008. **38**(2): p. 159-174.
22. Black, L., C. Breen, J. Yarwood, K. Garbev, P. Stemmermann, and B. Gasharova, *Structural features of C-S-H(I) and its carbonation in air-A Raman spectroscopic study. Part II: Carbonated phases.* Journal of the American Ceramic Society, 2007. **90**(3): p. 908-917.
23. Lange, L.C., C.D. Hills, and A.B. Poole, *The influence of mix parameters and binder choice on the carbonation of cement solidified wastes.* Waste Management, 1996. **16**(8): p. 749-756.
24. Gunning, P., C. Hills, and P. Carey, *Production of lightweight aggregate from industrial waste and carbon dioxide*. Vol. 29. 2009. 2722-8.
25. Shi, H.S. and L.L. Kan, *Leaching behavior of heavy metals from municipal solid wastes incineration (MSWI) fly ash used in concrete.* J Hazard Mater, 2009. **164**(2-3): p. 750-4.
26. Fernandez Bertos, M., S.J. Simons, C.D. Hills, and P.J. Carey, *A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2.* J Hazard Mater, 2004. **112**(3): p. 193-205.
27. Guo, X., H. Shi, K. Wu, Z. Ju, and W.A. Dick, *Performance and risk assessment of alinite cement-based materials from municipal solid waste incineration fly ash (MSWIFA).* Materials and Structures, 2015. **49**(6): p. 2383-2391.

CHAPTER 2. LITERATURE REVIEW AND BASIC DEFINITIONS

2.1. MUNICIPAL SOLID WASTE INCINERATION RESIDUES

Municipal Solid Waste (MSW) production is estimated at about 1 to 2 billion tons per year worldwide [1]. These wastes are being disposed of either by landfill or by incineration. As compared to landfill, incineration reduces the volume of waste by 90% and the mass by 70% and provides options to recover energy by generating electricity. Moreover, the incineration of MSW eliminates almost all organic compounds; this incineration is the obvious choice in areas where population densities are moderately high, and the landfill sites are limited [2]. However, the process is not popular because the municipal solid waste incineration (MSWI) generates residues. The incineration process can be divided into three major parts; incineration, energy recovery and air pollution control, the residues collected from these processes are termed the bottom ash, boiler ash and APC residues respectively [3]. APC residues are sometimes termed fly ash and APC lime. It is estimated that incineration of one ton of MSW produces 250 to 300 kg of bottom ash and 25 to 30 kg of air pollution control (APC) lime [4]. Special landfill sites are required to dispose of the APC lime. Because of the environmental concerns, the incineration accounts for only 5% of the total MSW disposal in Canada, and the majority of the MSW is still landfilled [5]. It is, therefore, imperative to develop a closed-loop clean incineration technology through the beneficial utilization of the MSWI residues.

2.2. THE COMPOSITION OF MSWI RESIDUES

The mineral composition of MSW varies from country to country, society to society and within the society over time. The MSWI ashes mineral composition depends on the raw composition of MSW [6]. The major elements of these MSWI residues are Ca, Si, Al, Fe, Mg, Cl, Na and K, and the common oxides are CaO, SiO_2, Na_2O, K2O, Al_2O_3, and SiO_2. The availability and amount of these minerals and oxides are dependent on the season and inhabitant of the country [6].

2.3. USE OF MSWI RESIDUES

2.3.1. GENERAL USE

Recycling and reusing are the best strategies for MSWI residues management. Although, these residues are rich in contamination such as heavy metal, salts, and organic metals. MSWI residues with the application of appropriate treatments could be used for different applications. Technical performance, environmental impact, and suitability of processing are the main factors which decide further possible applications [7]. MSWI residues show a potential use in different industries such as glasses and ceramic industry, agriculture, wastewater treatment, zeolite production and quite widely in the construction industry. APC residues are used to synthesized zeolite by the hydrothermal process, a higher concentration of heavy metals such as Zn and Pb were found in the residual liquid after the synthesis, therefore, further treatment is required before discharge. MSWI bottom ash is also used to synthesized zeolite, but this is less common than using APC residues for synthetization of zeolite [8]. Furthermore, MSWI bottom ash is beneficially used as an adsorbent and to remove heavy metals from wastewater [9]. Although MSWI bottom ash contains heavy metals and has leachability problems, due to the higher toxicity of the heavy metal, the presence of heavy metals in the water is a serious problem [10]. MSWI bottom ash is also used for purification of a gas, sulfur gas can be reduced by using MSWI bottom ash from a landfill gas [11]. In addition, APC residues have the potential to be used as an adsorbent for heavy metals, dyes and organics [12].

2.3.2. USE IN THE CONSTRUCTION INDUSTRY

MSWI residues can be used in the construction industry as well. MSWI residues are used to produced glasses, ceramics and glass-ceramics as they contain a high amount of SiO_2, CaO, and Al_2O_3. Ceramic tiles produced by using MSWI ashes up to 20% showed high compressive strength and low absorption of water; theses vitrified MSWI residues are used as raw material to produce glass-ceramics [13]. Another direct and simple method of MSWI ashes is to replace the base course of roads widely [14]. The MSWI ash stabilized by washing demonstrated better results than the cement stabilized ashes used in the road base courses [15]. MSWI ashes ware also used as aggregates in roads and concrete construction, APC residues are used successfully to produce lightweight aggerates [16].

2.3.3. USE IN CEMENT PRODUCTION

Several researchers have effectively used the MSW incineration (MSWI) residues to produce environmentally friendly cement. Cement produced using 15 % of MSWI residues as the raw material and sintering at 1400°C demonstrated very low compressive strengths of 7 MPa [17]. Shi et al. produced sulphoaluminate cement using 30% MSWI fly ash as a raw feed of cement clinkered at 1300 °C; with a 28-day cement paste compressive strength of 80 MPa [18]. Production of cement using 50% MSWI ash is demonstrated at pilot scale (50 tons/day), with the clinkering process being carried out in a rotary kiln at 1400°C; compressive strength of 35 MPa has been attained after 28-days of moist curing [19]. In addition, when the MSW fly ash is heated at 1450^{o}C, it forms a glassy slag, which can be used as a cementitious material to replace OPC [20]. In Japan, the hydraulic eco-cement was produced by mixing incineration ash with limestone at 1:1 ratio as raw feed material to produce clinkers in a cement kiln at 1350°C [21]. Zaid and Shao have successfully produced a carbonation activated cement binder by using a mixture proportion containing 85 % of MSWI residues at a clinkering temperature of 1000°C. The cement binder showed no hydraulic reactivity, but it achieved compressive strength of over 50 MPa with a carbon dioxide uptake capacity of about 7% [22].

2.4. ORDINARY PORTLAND CEMENT AND CONCRETE

Concrete is the second most consumed material in the world, with water being the most consumed material in the world [23]. In 2016, more than 4.2 billion metric tons of cement was produced, and this amount is projected to increase by 2.5 % annually [24]. Cement is very energy intensive and its production requires very large quantities of natural resources i.e. the production of each ton of cement requires more than 1.6 ton of natural resources, which are limited on planet earth. Burning of the fossil fuels to fulfill the energy required to produce cement and calcination of limestone emits a very high amount of CO_2, a ton of CO_2 is emitted during the production of each ton of cement. This is why the cement industry is the largest source of CO_2 emissions; cement industry emits about 5 % of total CO_2 emissions annually [25]. Accordingly, one of the major challenges for the concrete and cement industries is to find an alternative binding cementitious system with low carbon emissions as compared with the OPC. The carbon footprint can be reduced by using alternative fuels, use of supplementary cementitious materials, carbon capture and storage, and production of alternative cements.

2.5. ALTERNATIVE CEMENTS

Many alternative cementitious systems with lower carbon footprint have been reported during the past decade [26]. Low-hydraulic to non-hydraulic calcium-silicate cements are one of the most recent additions to the low carbon footprint alternative clinker systems [27]. These binders are composed of wollastonite ($CaO.SiO_2$) and rankinite ($3CaO.2SiO_2$) which are low-lime calcium silicates [28]. These cements are produced at lower energy levels and the major component is belite as compared with the OPC which have alite as the major component. Due to the lack of hydraulic reactivity of belite as compared with alite, it has been considered as an undesirable component of the OPC. However, the belite is found to exhibit enhanced reactivity in the presence of CO_2 [29]. When subjected to accelerated carbonation, these binder systems can store CO_2 up to 17 % (by mass) in the case of calcium silicate cements [30]. Production of these cement binders at lower temperatures, along with the CO_2 storage capacity, and the overall carbon footprint of concrete is smaller than that for the OPC concrete; the carbon footprint of carbonated CSC concrete has been reported to be about 70% of OPC concrete [28].

2.6. CARBONATION CURING

Carbonation activation is a chemical reaction between CO_2 and tri-calcium silicate ($3CaO\cdot SiO_2$ or C_3S) and/or dicalcium silicate ($2CaO\cdot SiO_2$ or C_2S) in the cement paste. Carbonation of calcium-silicate system is a sequence of reactions; adequate hydration is indispensable to ease the carbonation reactions as most of the reactions fall in the aqueous phase. Carbonic acid forms after the hydration of CO_2 gas, which ionizes by liberating HCO_3^-, CO_3^- and H^+ ions, decreasing the pH of solution instantly, which accelerates the dissolution of calcium silicates and releases the SiO_4^{2-} and Ca^{2+} ions in the solution. Under these thermodynamic conditions, these ions recombine and nucleates the C-S-H and calcium carbonate simultaneously [31]. The chemical reaction is explained in Equation 2.1 and 2.2. Equation 2.2 governs the carbonation behavior of belite cement. Immediately after casting, CO_2 is deliberately introduced to fresh cement paste, producing the hybrids of calcium silicate hydrate ($3CaO\cdot 2SiO_2\cdot 3H_2O$ or CSH) and calcium carbonate ($CaCO_3$) as a result [32]. Due to this depletion of calcium hydroxide ($Ca(OH)_2$), the carbonated concrete products can perform better in term of durability, strength, dimensional stability as compared with the normal concrete. The best application of early age carbonated concrete is in the manufacturing of concrete bricks/blocks and unreinforced precast concrete products.

$$2(3CaO\cdot SiO_2) + 3CO_2 + 3H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + 3CaCO_3 \quad (2.1)$$

$$2(2CaO\cdot SiO_2) + CO_2 + 3H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + CaCO_3 \quad (2.2)$$

A comprehensive study on performance improvement and CO_2 utilization for the precast concrete product has been carried out. In this study, a variety of precast OPC concrete products, such as concrete pipes, concrete masonry units, and concrete hollow-core slabs were investigated for their capacities to uptake CO_2. The results showed that the early age carbonation activation improves early age strength, and the resistance to freeze-thaw, chloride ion penetration, sulfate attack, resistance to acid attack [33].

2.7. ENVIRONMENTAL IMPACT OF MSWI RESIDUES

In addition to the valuable minerals and oxides, these MSWI residues also contain heavy metals, dioxins, and organic compounds. MSWI residues contain Cr, Cu, Hg, Cd, Zn, Ni, and Pb, usually, Pb and Zn exist in the largest proportions. Generally, fly ash contains higher amounts of metals as compared with the bottom ash due to vaporization of the metals during combustion [34]. MSWI bottom ashes contain a smaller amount of chlorine as compared with the MSWI fly ash. The presence of a scrubber in the air pollution control system could be the possible reason. The acidic gasses, such as HCl removed by these scrubbers, causes an increase of chlorine in the APC residues. MSWI bottom ash has the loss on ignition 3-5%, while and fly ash demonstrates a loss on ignition in the range of 4-13% [13, 35]. The international standards for dioxin emission in the flue gas are 0.1 ng I-TEQ/m^3. The Japan Ministry of Environment limits the dioxin levels in soils to 1 ng I-TEQ/g. In most countries, the MSWI flash ash values exceed the Japanese values for dioxin [36]. Activated carbon injections are used to adsorb dioxin; the lime scrubbers remove the dioxin by changing the vapor phase to solid phase [37]; the APC residues are classified as hazardous waste as they contain relatively high amounts of dioxin [38, 39]. The dioxin and furans formation can be reduced by different methods during incineration of MSW, proper combustion of MSW and the better designed APC are the effective ways to control dioxin and furans. If combustion of MSW takes place above 1000°C with a resistance time of more than 1second and turbulence of the combustion chamber greater than a Reynold number 50,000, this will help to decrease the formation of dioxins. The reduction of formation or minimization of dioxin in the flue gas can be boosted by cooling the flue gas from 400°C to 250 °C and lime scrubbers [38].

2.8. MSWI RESIDUES STABILIZATION

To reduce the environmental impact by utilizing the MSWI residues, many methods are adopted. Thermal treatment and accelerated carbonation are commonly used in treatment methods.

2.8.1. THERMAL TREATMENT

The thermal process can decrease the toxic contamination; the high temperature of 1400°C will effectively expel the dioxin and furans [40]. Bottom ash could be used after the fusion and vitrification, and vitrification of APC residues can recover almost all the toxic heavy metals and completely detoxify the residues [41]. The vitrified bottom ash shows lower leachability as compare with the original bottom ash. Although vitrification is very energy intensive and expensive, it can be a sustainable option for MSWI residue treatment [42]. Moreover, MSWI bottom ash and APC ashes could be heavily loaded with chlorine and need to be fixed. The past research has shown that high-temperature clinkering could bind these chlorides into a stable structure, followed by the hydration process which further reduces the amount of soluble chlorides due to retention within the hydrated products [43].

2.9. ACCELERATED CARBONATION PROCESS

Hazardous waste can be treated very effectively by the accelerated carbonation process. Leaching of heavy metals, which are part of MSWI residues, can be reduced by early age carbonation treatment of the cement produced using MSWI ashes. The volume expansion is associated with the formation of $CaCO_3$, which helps in the reduction of porosity and in the withholding of heavy metals [44]. The mobility of certain heavy metals, such as Pb, Zn, Cu, Cd, and Cr can be reduced, or regulated by neutralization of pH caused by the formation of carbonate minerals [45]. Carbonation is quite often used in waste treatment to reduce leaching of heavy metals quantity before undertaking any landfill [46].

2.10. SUMMARY

A review of the literature on topics related to this thesis is briefly summarized in this chapter. It was recognized that there were several challenges for promoting the reuse of MSWI residues. This research aimed to study the feasibility of producing an eco-cement from MSWI residue and carbon dioxide. Three tasks were proposed to achieve the objective of eco-cement production.

1. **Task 1** is to develop eco-cement from MSWI residues. The target is to make eco-cement with waste ranging from 90% to 100%. Comprehensive parametric testing is planned to optimize the production of eco-cement in terms of energy, time and economy.
2. **Task 2** is the characterization of eco-cement. The microstructural characterization studies, for the clinker phases of eco-cement and the phases developed after the carbonation, are designed extensively.

3. **Task 3** is to synthesize the CO_2 reactive phases for the improved understanding of strength development mechanisms of eco-cement.
4. **Task 4** is to assess the environmental impact of eco-cement, detailed environmental testing is designed to observe the impact of all the hazardous materials present in the MSWI residues.

REFERENCES

1. Hoornweg, D. and P. Bhada-Tata, *What a waste: a global review of solid waste management.* What A Waste: A Global Review of Solid Waste Management, 2012.
2. Stehlík, P., *Contribution to advances in waste-to-energy technologies.* Journal of Cleaner Production, 2009. 17(10): p. 919-931.
3. Lee, V.K.C., K.C.M. Kwok, W.H. Cheung, and G. McKay, *Operation of a municipal solid waste co-combustion pilot plant.* Asia-Pacific Journal of Chemical Engineering, 2007. 2(6): p. 631-639.
4. Aubert, J.E., B. Husson, and A. Vaquier, *Use of municipal solid waste incineration fly ash in concrete.* Cement and Concrete Research, 2004. 34(6): p. 957-963.
5. Canada, S. *Waste Management Industry Survey*. [Online] 2006 [cited 2018 August 20, 2018]; Available from: https://www150.statcan.gc.ca/n1/pub/16f0023x/16f0023x2013001-eng.htm.
6. He, P.J., H. Zhang, C.G. Zhang, and D.J. Lee, *Characteristics of air pollution control residues of MSW incineration plant in Shanghai.* Journal of Hazardous Materials, 2004. 116(3): p. 229-237.
7. Ferreira, C., A. Ribeiro, and L. Ottosen, *Possible applications for municipal solid waste fly ash.* Journal of Hazardous Materials, 2003. 96(2-3): p. 201-216.
8. Penilla, R.P., A.G. Bustos, and S.G. Elizalde, *Zeolite Synthesized by Alkaline Hydrothermal Treatment of Bottom Ash from Combustion of Municipal Solid Wastes.* Journal of the American Ceramic Society, 2004. 86(9): p. 1527-1533.
9. Gupta, V.K., I. Ali, V.K. Saini, T. Van Gerven, B.D. Van Bruggen, and C. Vandecasteele, *Removal of dyes from wastewater using bottom ash.* Industrial and Engineering Chemistry Research, 2005. 44(10): p. 3655-3664.
10. Ho, Y.S. and G. McKay, *Comparative sorption kinetic studies of dye and aromatic compounds onto fly ash.* Journal of Environmental Science and Health, Part A, 1999. 34(5): p. 1179-1204.

11. Ducom, G., D. Radu-Tirnoveanu, C. Pascual, B. Benadda, and P. Germain, *Biogas – Municipal solid waste incinerator bottom ash interactions: Sulphur compounds removal.* Journal of Hazardous Materials, 2009. 166(2): p. 1102-1108.
12. Polowczyk, I., A. Bastrzyk, T. Koźlecki, W. Sawiński, P. Rudnicki, A. Sokołowski, and Z. Sadowski, *Use of fly ash agglomerates for removal of arsenic.* Environmental Geochemistry and Health, 2010. 32(4): p. 361-366.
13. Yang, J., B. Xiao, and A.R. Boccaccini, *Preparation of low melting temperature glass-ceramics from municipal waste incineration fly ash.* Fuel, 2009. 88(7): p. 1275-1280.
14. François, D. and K. Pierson, *Environmental assessment of a road site built with MSWI residue.* Science of The Total Environment, 2009. 407(23): p. 5949-5960.
15. Mulder, E., *Pre-treatment of mswi fly ash for useful application.* Waste Management, 1996. 16(1-3): p. 181-184.
16. Cinquepalmi, M.A., T. Mangialardi, L. Panei, A.E. Paolini, and L. Piga, *Reuse of cement-solidified municipal incinerator fly ash in cement mortars: Physico-mechanical and leaching characteristics.* Journal of Hazardous Materials, 2008. 151(2): p. 585-593.
17. Shih, P.H., J.E. Chang, and L.C. Chiang, *Replacement of raw mix in cement production by municipal solid waste incineration ash.* Cement and Concrete Research, 2003. 33(11): p. 1831-1836.
18. Shi, H.s., K. Deng, F. Yuan, and K. Wu, *Preparation of the saving-energy sulphoaluminate cement using MSWI fly ash.* Journal of Hazardous Materials, 2009. 169(1-3): p. 551-555.
19. Kikuchi, R., *Recycling of municipal solid waste for cement production: Pilot-scale test for transforming incineration ash of solid waste into cement clinker.* Resources, Conservation and Recycling, 2001. 31(2): p. 137-147.
20. Lee, T.-C., W.-J. Wang, P.-Y. Shih, and K.-L. Lin, *Enhancement in early strengths of slag-cement mortars by adjusting basicity of the slag prepared from fly-ash of MSWI.* Cement and Concrete Research, 2009. 39(8): p. 651-658.
21. Ampadu, K.O. and K. Torii, *Characterization of ecocement pastes and mortars produced from incinerated ashes.* Cement and Concrete Research, 2001. 31(3): p. 431-436.

22. Ghouleh, Z. and Y. Shao, *Turning municipal solid waste incineration into a cleaner cement production.* Journal of Cleaner Production, 2018. 195: p. 268-279.

23. Development, W.B.C.f.S., *Cement Technology Roadmap 2009: Carbon Emissions Reductions Up to 2050*. 2009.

24. Shen, L., T. Gao, J. Zhao, L. Wang, L. Wang, L. Liu, F. Chen, and J. Xue, *Factory-level measurements on CO2 emission factors of cement production in China.* Renewable and Sustainable Energy Reviews, 2014. 34: p. 337-349.

25. Scalenghe, R., F. Malucelli, F. Ungaro, L. Perazzone, N. Filippi, and A.C. Edwards, *Influence of 150 years of land use on anthropogenic and natural carbon stocks in emilia-romagna region (Italy).* Environmental Science and Technology, 2011. 45(12): p. 5112-5117.

26. Gartner, E. and T. Sui, *Alternative cement clinkers.* Cement and Concrete Research, 2017.

27. Riman, R.E., T.E. Nye, V. Atakan, C. Vakifahmetoglu, Q. Li, and L. Tang, *Synthetic formulations and methods of manufacturing and using thereof.* Synthetic Formulations and Methods of Manufacturing and Using Thereof, 2015.

28. Sahu, S. and N. DeCristofaro, *Solidia Cement™, Solidia Technologies. White Paper.* 2013.

29. Ashraf, W. and J. Olek, *Carbonation behavior of hydraulic and non-hydraulic calcium silicates: potential of utilizing low-lime calcium silicates in cement-based materials.* Journal of Materials Science, 2016. 51(13): p. 6173-6191.

30. Ashraf, W., J. Olek, and V. Atakan. *Carbonation reaction kinetics, CO2 sequestration capacity, and microstructure of hydraulic and non-hydraulic cementitious binders*. in *Sustainable Construction Materials and Technologies*. 2016.

31. Fernández Bertos, M., S.J.R. Simons, C.D. Hills, and P.J. Carey, *A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2.* Journal of Hazardous Materials, 2004. 112(3): p. 193-205.

32. Young, J.F., R.L. Berger, and J. Breese, *Accelerated Curing of Compacted Calcium Silicate Mortars on Exposure to CO2.* Journal of the American Ceramic Society, 1974. 57(9): p. 394-397.

33. El-Hassan, H., Y. Shao, and Z. Ghouleh, *Effect of Initial Curing on Carbonation of Lightweight Concrete Masonry Units*. Vol. 110. 2013. 441-450.

34. Chang, C.Y., C.F. Wang, D.T. Mui, M.T. Cheng, and H.L. Chiang, *Characteristics of elements in waste ashes from a solid waste incinerator in Taiwan.* Journal of Hazardous Materials, 2009. 165(1-3): p. 766-773.

35. Saikia, N., S. Kato, and T. Kojima, *Production of cement clinkers from municipal solid waste incineration (MSWI) fly ash.* Waste Management, 2007. 27(9): p. 1178-1189.

36. Bie, R., S. Li, and H. Wang, *Characterization of PCDD/Fs and heavy metals from MSW incineration plant in Harbin.* Waste Management, 2007. 27(12): p. 1860-1869.

37. Lee, V.K.C., W.H. Cheung, and G. McKay, *PCDD/PCDF reduction by the co-combustion process.* Chemosphere, 2008. 70(4): p. 682-688.

38. McKay, G., *Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: Review.* Chemical Engineering Journal, 2002. 86(3): p. 343-368.

39. Zhang, H.J., Y.W. Ni, X.P. Zhang, Q. Zhang, L. Zhao, N. Zhang, and J.P. Chen, *PCDD/F formation and its mass balance in a MSW incineration system.* Huanjing Kexue/Environmental Science, 2008. 29(4): p. 1133-1137.

40. Rui Lima , M.S., *Technical Note: An effective thermal technology for the detoxification of MSW fly ash.* Int. J. Environ. Technol. Manage, 2003. Volume 3(Issue 2): p. 212-218.

41. Izumikawa, C., *Metal recovery from fly ash generated from vitrification process for MSW ash.* Waste Management, 1996. 16(5): p. 501-507.

42. Xiao, Y., M. Oorsprong, Y. Yang, and J.H.L. Voncken, *Vitrification of bottom ash from a municipal solid waste incinerator.* Waste Management, 2008. 28(6): p. 1020-1026.

43. Guo, X., H. Shi, K. Wu, Z. Ju, and W.A. Dick, *Performance and risk assessment of alinite cement-based materials from municipal solid waste incineration fly ash (MSWIFA).* Materials and Structures, 2015. 49(6): p. 2383-2391.

44. Lange, L.C., C.D. Hills, and A.B. Poole, *The influence of mix parameters and binder choice on the carbonation of cement solidified wastes.* Waste Management, 1996. 16(8): p. 749-756.

45. Shi, H.S. and L.L. Kan, *Leaching behavior of heavy metals from municipal solid wastes incineration (MSWI) fly ash used in concrete*. J Hazard Mater, 2009. 164(2-3): p. 750-4.

46. Fernandez Bertos, M., S.J. Simons, C.D. Hills, and P.J. Carey, *A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2*. J Hazard Mater, 2004. 112(3): p. 193-205.

CHAPTER 3. PRODUCTION OF ECO-CEMENT USING MSW INCINERATION ENERGY AND RESIDUES

PREFACE

A summary of the literature was presented in Chapter 2. Cement binders derived from the municipal solid waste incineration (MSWI) residues in the past were produced either at high clinkering temperatures or utilized the limited quantities of MSWI residues. This study focused to make eco-cement from MSWI residues using as much as possible the residues. The target was to make eco-cement with waste ranging from 90% to 100% and to produce the eco-cement at lower clinkering temperature around 1000°C to 1100°C to able production of the future eco-cement in an incinerator, rather at a cement kiln in a cement plant. In this case, an incinerator can be converted into environmentally friendly cement production. The results of the various experimental studies to the derivation of eco-cement from MSWI residues are presented in this chapter. The performance criteria for the eco-cement are the higher compressive strength and CO_2 uptake. Different mixing proportions were used to maximize the MSWI residues content. Multiple blending methods were used to achieve improved mixing of the proportioned MSWI residue; the effects of clinker size on the performance of eco-cement is also studied. The effect of clinkering temperatures is also examined to develop a recommendation for future studies. Eco-concrete was produced to confirm the binding properties of eco-cement. Finally, the basic leeching tests are performed to confirm the environmentally safety of eco-cement.

3.1. ABSTRACT

Municipal solid waste (MSW) incineration is an effective way to reduce the volume of wastes while producing energy. The challenge is the management of the residues, namely, air pollution control (APC) lime, the boiler ashes and the bottom ashes, created as by-products of the process. This study is to examine a novel approach to the innovative use of both incineration energy and residues to produce an ecological cement which can be activated by introducing carbon dioxide. It is noted that if eco-cement is made exclusively from 100% incineration ashes, it would turn out to be less carbon-reactive and more latent hydraulic. If the eco-cement is proportioned with 6 % virgin material as an additive, the material is more carbon-reactive along with higher early strength. The effect of the process parameters on the performance of eco-cement is investigated. This novel cementitious material demonstrated a compressive strength of 55 MPa after two hours of carbonation activation which is quite comparable to that of ordinary Portland cement (OPC). The CO_2 uptake through the carbonation activation is about 7%, based on the cement content and the leaching test shows the heavy metal contents are well under the regulatory limits. In the near future, eco-cement can be produced in an MSW incinerator with a maximum clinkering temperature of 1100°C, and incineration residues as raw meals. The concrete made from eco-cement can be activated by carbon dioxide captured from the incinerator stack to accelerate early strength and sequester the carbon dioxide for emission reduction.

Keywords: Municipal solid waste incineration, bottom ash, air pollution control ashes, eco-cement, recycle, conservation.

3.2. INTRODUCTION

Every year billions of tons of solid wastes are produced by municipalities around the world. The municipal solid wastes (MSW) are being disposed of either in landfills or by incineration. As compared to the landfills, incineration reduces the volume of waste by 90% and the mass by 70%, with an option to produce energy by generating electricity. The incineration of MSW eliminates almost all organic compounds; however, the process is not popular because of the municipal solid waste incineration (MSWI) residues generated. It is estimated that incineration of one ton of MSW produces 250 to 300 kg of bottom ash and 25 to 30 kg of air pollution control (APC) lime [1]. Special landfill sites are required to dispose of the APC lime. Because of the environmental concerns, the incineration accounts for only 5% of total MSW disposal in Canada, and the majority of the MSW is still being landfilled [2]. It is, therefore, imperative to develop a closed-loop clean incineration technology through the beneficial utilization of the MSWI residues.

In European countries, more than 50% of bottom ashes are used in roads as a base material, in concrete and asphalt pavements [3]. In Japan, the hydraulic eco-cement is produced by mixing incineration ash with limestone in a 1:1 ratio as raw feed material to produce clinker in a cement kiln at 1350˚C [4]. In China, MSWI fly ash is used up to 16% as raw material at 1450˚C in making Portland cement [5]. In addition, when the MSW fly ash is heated at 1450˚C, it forms a glassy slag, which can be used as a cementitious material to replace OPC [6]. A number of studies showed that MSWI fly ash could be used as a raw meal up to 44 % with other virgin materials such as $CaCO_3$, SiO_2 and Fe_2O_3 to produce cement clinker at 1450°C in a cement kiln [5, 7].

It is interesting to know if such cement can be produced in the incinerator at 1100 ˚C. This will be typically low energy cement, which can be produced at a clinkering temperature from 1000 ˚C to 1200 ˚C. These low-energy cements are basically belite cements because of the formation of large quantities of dicalcium silicate (C_2S) at lower temperature [8]. Production of cement at lower temperature produces β-C_2S as a latent hydraulic and γ-C_2S as a non-hydraulic. To improve the hydraulic performance of low-energy cements, β-C_2S can be well-maintained in a metastable state by providing the right cooling environment and proper crystal size [9]. Cement produced after heating above 1000°C temperature and rapid quenching can convert γ-C_2S to β-C_2S. To make belite cement useful and comparable to OPC, a high initial strength that is comparable to hydrated OPC strength can be achieved through activating β-C_2S and γ-C_2S by carbonation curing at an early age [10].

Carbonation activation is a chemical reaction between CO_2 and tri-calcium silicate ($3CaO\cdot SiO_2$ or C_3S) and/or dicalcium silicate ($2CaO\cdot SiO_2$ or C_2S) in the cement paste. The chemical reaction is explained in Equation 3.1 and 3.2. Equation 3.2 governs the carbonation behavior of belite cement. Immediately after casting, CO_2 is deliberately introduced to fresh cement paste. The hybrids of calcium silicate hydrate ($3CaO\cdot 2SiO_2\cdot 3H_2O$ or CSH) and calcium carbonate ($CaCO_3$) are produced as a result of the carbonation process [11]. Due to the depletion of calcium hydroxide ($Ca(OH)_2$), the carbonated concrete products can perform better in term of durability, strength, dimensional stability as compared with regular concrete. The best application of early age carbonated concrete is the manufacturing of concrete bricks/blocks and unreinforced precast concrete products.

$$2(3CaO\cdot SiO_2) + 3CO_2 + 3H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + 3CaCO_3 \qquad (3.1)$$

$$2(2CaO\cdot SiO_2) + CO_2 + 3H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + CaCO_3 \qquad (3.2)$$

A comprehensive study of performance improvement and CO_2 utilization for the precast concrete product was carried out. A variety of precast OPC concrete products, such as concrete pipes, concrete masonry units, and concrete hollow-core slabs were investigated for their capacity for

CO_2 uptake. The results showed that the early age carbonation activation improves early age strength, and the resistance to freeze-thaw, chloride ion penetration, sulfate attack, resistance to acid attack, [12, 13].

Leaching of heavy metals, which are part of MSWI residues, can be further reduced by early age carbonation treatment of cement produced using MSWI ashes. The volume expansion is associated with the formation of $CaCO_3$, which helps in the reduction of porosity and in the withholding of heavy metals [14]. The mobility of certain heavy metals, such as Pb, Zn, Cu, Cd, and Cr can be reduced, or regulated by the neutralization of pH caused by the formation of carbonate minerals due to carbonation activation [15, 16]. Carbonation is quite often used in waste treatment to reduce leaching of heavy metals quantity before landfill [17]. MSWI bottom ash and APC ashes could be heavily loaded with chlorine and need to be fixed. Past research has shown that the high-temperature clinkering could bind these chlorides into a stable structure at first and followed by the hydration process further reduces the amount of soluble chlorides due to their retention in the hydrated products [18].

All previous work on MSWI ash-based cement was performed in a traditional cement kiln in a cement plant using a maximum of 50% MSWI bottom ash and APC fly ash as a raw meal, and a clinkering temperature higher than 1300 °C. Attempts were made to produce eco-cement at incineration temperature with 85% incineration residues from a Quebec incinerator [22]. This research continues the study of producing eco-cement by using 100% MSWI residues from an Ontario incinerator at incineration temperature of 1100°C. The effect of material proportions and process parameters on the performance of eco-cement to examined for full-scale production. If successful, the eco-cement can be produced at incinerator using all MSWI residues collected at the site and the incineration heat for clinkering to turn an incineration process into a clean production of cement. The principal challenge about the cement produced at 1100°C is about its very low to non-hydraulic behavior. To counter this problem, carbonation activation will be used in strength development. Which accelerates the early strength development of a low energy cement and sequesters a certain amount of carbon dioxide in ecological cement products to reduce carbon emissions from an incineration practice. This research emphasizes the conservation of energy and environment by using MSWI residues as a resource to produce environmentally friendly cement and sustainable concrete products as compared with the regular concrete.

3.3. MATERIALS AND METHODOLOGY

3.3.1. MATERIAL

The MSW incineration residues used in this research program were collected from Emerald Energy from Waste (EFW) in Brampton, Ontario. The incineration process flow diagram of the Emerald-EFW plant is shown in Fig. 3.1. The combustion furnace has two compartments: a lower chamber (temperature between 750-900˚C) and an upper chamber (at a maximum temperature of 1050˚C). The upper chamber will be investigated for its potential to serve as a furnace for making eco-cement. There is a total of five such furnaces working in series at the facility. Approximately 180,000t of MSW are incinerated annually, leaving behind 30,000t of bottom ash, 500t of vitrified boiler ash and 4,000t of air pollution control (APC) lime residues. Hydrated lime and ground silica sand were used as supplementary additives when needed. Lafarge® ordinary Portland cement was marked as the reference material.

3.3.2. MATERIAL PREPARATION

All the collected residues were dried at 105°C for 24 hours. The APC residues were in powder form and had a very fine particle size. As-received bottom ash had some metal contents and had a wide range of particle sizes. The bottom ash was sieved on 10 mm size sieve to remove metals. The boiler ash had a very wide range of particle size, it was also sieved on 10 mm sieve to remove large particles. The particle size analysis was carried out using a HORIBA LA-920 particle size analyzer, the material powders were dispersed in isopropanol; the particle size curves are shown in Fig. 3.2. It was observed that the APC residues without sieving had very fine particles, and after the sieving boiler, ash and bottom ash particle, the sizes were fairly analogs.

3.3.3. COMPOSITIONAL ANALYSIS

The chemical compositions of the MSWI residues were determined by X-Ray Fluorescence (XRF) analysis using a Panalytical PW2440 spectrometer (MagiX PRO Series). Sulfur and carbon contents were measured by using an ELTRA CS-800 Carbon/Sulfur Analyzer. The loss on ignition (LOI) was measured in accordance with ASTM D7348. The XRF composition of MSWI residues and regular OPC is summarized in Table 3.1. The cone-and-quartering sampling technique was implemented to ensure that the analyzed samples show the contiguous possible material representativeness. This process contains making a heap of material, flattening, and dividing into four equal quarters. was shaped into a cone, flattened and then divided into four equal quarters. The next step would be to retain two opposite quarter and discard the other two, and the process would be repeated until getting the required amount of sample is obtained. This process was repeated for each residue, and finally, 20 g of material samples were collected for analysis.

3.4. RAW MIX PREPARATION

It was observed from the XRF analysis results that three major oxides required for cement production i.e. CaO, SiO_2, Al_2O_3, are available in the ashes in a comparable amount to Portland cement composition. However, the main concern in the MSWI residues is chlorine, which is present in a very large quantity. The main goal was to fulfill the compositional requirements for belite formation by adding minimum possible commercial materials. After several trials, two blends were chosen, one with the hundred percent MSWI residues as a raw meal and the second with only 5.37 % commercial additives. After deciding the mix proportions, the blending of the raw blends was a critical step because the quality of the product largely depends on the blending of proposed mixes. To achieve uniform blending, different blending mechanisms experimented and the most efficient mix in terms of uniformity, practicality, and economy was adopted for the next step of the cement production process. Nodulizing was the next step in the eco-cement production line; it was carried out using a mechanical nodule maker. The nodules were the feed material for the clinkering or the heat treatments.

3.5. CLINKERING

Clinkering was the most important factor in the production line of eco-cement. Lindberg/Blue-M muffle furnace (model: BF51634PC-1) was used to simulate the clinkering process that would be performed in the incinerator in the future. To study the effect of temperature on cementitious properties of the clinker, a range of five different clinkering temperatures (1000, 1050, 1100, 1150, and 1200°C) was chosen, with all the temperature being below the conventional temperature of 1450°C. The temperature for 1-hour clinkering was adopted to achieve the desired final cementitious properties for the subsequent clinkering trials. Clinkers were then pulverized to a cement-like powder with a broad particle size range by utilizing minimum grinding energy to make it more energy efficient. The particle size distribution curve is presented in Fig. 3.2, the particle size varied from 0.3 microns to 300 microns, but maximum particle size was distributed around 100 microns.

The production process of eco-cement is shown schematically in Fig. 3.3. Sieving and drying of as-received MSWI residues were the starting steps of the production process. MSWI residues were then proportioned according to the proposed clinker blend and mixed to achieve homogeneity of the blend. After exhaustive mixing, the blend was pulverized to a fine powder by a ring-and-puck vibratory pulverizer. The pulverizing time was adjusted to economize the production in terms of energy and time saving, and without compromising the performance the of eco-cement. The pulverized powder was used to produce nodules for thermal treatment using a mechanical rotating nodule producing machine. The powder was added to the machine, and water was sprinkled over the powder; water to cement ratio of 0.15 was used. The machine was operated at 35 rpm, and the process was continued until the spherical nodules were formed. These nodules were then placed in an aluminum boat shaped crucible, and the crucible was positioned in the furnace for clinkering, which was carried out at different temperatures and for different times; the economical temperature and duration were chosen for further production. After the desired clinkering process, the clinkers were left inside the furnace to cool down slowly. After reaching the room temperature, the clinkers were retrieved from the furnace and pulverized again to produce eco-cement. The clinkering pulverizing time was optimized to achieve the desired performance economically. The entire production line and all the parameters were designed and optimized by sighting the large-scale production. All the parameters were decided based on practicality, ease, economy and in-line with the incinerator without compromising the performance of eco-cement.

3.6. PREPARATION OF CYLINDRICAL COMPACTS

The performance of the eco-cement was evaluated in terms of compressive strength and carbon uptake. For evaluation purposes, the resulting eco-cement was mixed with water using water-to-solid ratios (w/s) 0.1. Cylindrical compacts (diameter = 15mm, height = 30mm) were produced using a mold and uniaxial compression load of 5MPa; each compact cylinder was produced using 10 g of moistened eco-cement and a uniform 1-to-2 aspect ratio was achieved.

3.7. CARBONATION ACTIVATION OF COMPACTS

Carbonation of the eco-cement compacts was carried out at 152 kPa (22 psi) in an air-tight vessel, using pure CO_2 (99.5%) to simulate the recovered carbon dioxide from the flue gas for durations ranging from 2 to 24 hours. The carbonation results (weight gain and carbon uptake) were calculated by weighing compacts before and after carbonation. Non-carbonated hydration-cured samples were used as a reference for comparison at the age of 7, 28 and 90 days. After completing curing, the respective cylinders were immediately tested for compressive strength using an MTS-SINTECH 30/G Compressive Tester equipped with a 150kN load cell, in accordance with ASTM C-39. Each strength reading represented an average of the strength 5 cylinders.

3.8. ANALYSIS OF CLINKERS AND REACTION PRODUCTS

3.8.1. X-RAY DIFFRACTION MEASUREMENTS

To identify the mineral phases formed and their relative weight percentages were determined by quantitative X-ray diffraction (QXRD). The QXRD patterns of the eco-cement and the paste were recorded with Cu Kα radiation on a Siemens D-500 diffractometer. The diffraction pattern was obtained for the range of 2θ angles from 10° to 90° using the step size of 0.02. Eco-cement and cylindrical compacts prepared and cured (Section 3.6) were ground to powder form to perform QXRD analysis.

3.8.2. THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA was conducted to determine the composition of the various phases and to predict their thermal stability. Carbonation activated paste samples were crushed and then sieved through number 200 sieve (0.074 mm opening). Commercially available instrument (TA instrument TGA Q500) was used to perform the TGA test. The powdered sample was first kept in isothermal condition for 10 min and then the temperature was raised at the rate of 10 °C per minute up to 1000 °C. Approximately 5 to 10 mg of the powder samples were tested. Helium was used as purge gas during TGA tests.

3.8.3. SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

SEM was used to study the morphology of the samples and was performed on cylindrical paste specimens. The test specimens were dried and impregnated with epoxy. These compacts were randomly broken, a small piece from the broken surface was taken and four nano-meter coating of platinum was applied to avoid charging effects at high magnifications. Once prepared, the specimens were investigated using SEM, equipped with an energy dispersive X-ray (EDX) spectrometer, operated either in the backscattered electron (BSE) or the secondary electron (SE) modes, depending on the type of examinations performed.

The SEM images and the EDs were obtained by FEI Inspect F50 Field Emission Scanning Electron Microscope (FESEM) operating in a high vacuum mode with an accelerating voltage of 15 kV and using the working distance of 10.00 mm. Along with the SE images collected at different magnification levels, the EDS spectra were also acquired from selected individual points to perform the quantitative X-ray microanalysis. The energy-dispersive spectrometer measures the number and the energy of the X-rays emitted from a specimen. The energies of the X-rays are characteristic of the given chemical element and thus EDS allows for the determination of the elemental composition of the specimen.

3.9. ENVIRONMENTAL STABILITY OF ECO-CEMENT

Leaching of heavy metals from eco-cement was one of the important matters in this research program. To investigate the leachability of heavy metals from eco-cement, Environmental Protection Agency (EPA) Tests Method 1311 (Toxicity Characteristic Leaching Procedure, TCLP was conducted for three materials: raw blend for before clinkering, eco-cement, and carbonated eco-cement. TCLP was used to simulate municipal landfill exposure conditions. Leachate solutions were tested for concentrations of regulated heavy metals As, Ba, Cd, Cr, Pb, Se, Ag, and Hg. These environmental Tests were conducted by third-party EPA-accredited laboratory ALS global, Mississauga, Canada.

3.10. ECO-CONCRETE WITH ECO-CEMENT AND GRANITE AGGREGATES

The binding potential of the ecological cement was practically assessed from its consolidation strength of concrete. Concrete slabs of dimensions 50 x 50 x 30 mm were prepared according to the mix-design for concrete masonry units (CMU): 79% aggregates, 15% binder, 6% water (water-to-binder ratio, w/b = 0.40). Lafarge® general-use OPC was used as the commercial reference binder. The aggregate material was granite and used in its saturated surface dry (SSD) state. The maximum aggregate size was 6 mm and with a fineness modulus of 3.73.

Eco-cement-based concrete and OPC-based concrete both were cast into 50x50x30 mm slabs, consolidated by vibration and carbonation cured. Carbonation activation was carried out in a pressure vessel for 2 hours at 1.5 bar using high-purity CO_2 gas. Prior to carbonation, these slabs were preconditioned by air-drying to remove 30 – 40 % of the mix water to facilitate carbon dioxide gas diffusion. The assessment was made on compressive strength, using an MTS-SINTECH 30/G Compressive Tester equipped with a 150 KN load cell, in accordance with ASTM C39.

3.11. RESULTS AND DISCUSSIONS

3.11.1. EFFECT OF PROCESSING PARAMETERS ON THE STRENGTH OF ECO-CEMENT

3.11.1.1. EFFECT OF POWDER BLENDING

Three different blending techniques were employed to blend the raw materials: mortar mixer, rotating ball mill, and turnover ball mill. The other parameters were kept constant such as nodule size and clinkering temperature. The purpose behind trying different techniques was to find the best blending method which must be economical and energy efficient. The details of each blending method are given in Table 3.3.

From Fig. 3.4, the results indicated that the turnover ball mill method showed better results as compared to the other techniques. The mortar mixer blending method was least effective methods because the densities of MSWI residues were different i.e. bottom ash 2.3g/cm^3 and boiler ash 2.5g/cm^3 APC lime 0.7 g/cm^3. The boiler ash and bottom ashes tend to settle at the bottom of the mixer, and APC residues were dusting out throughout the blending process. Rotating ball mill solved the issue of scattering, but the particles were rotating in a specific rotation area, this process improved the blending than the mortar mixer. Turning the material over while rotating showed the best blending of the mixture. In this process the particles were changing the position during each rotation and turn, it was somehow a type of 3-D mixing. Based on these results, the turn-over ball mill blending technique was adopted for the future cement production process. Exhaustive mixing was the key factor for the better quality and higher strength of cement produce because it reduced the probability of localized lumps of material and helped in the homogeneous distribution of material. Homogenous raw mix leads to the consistent formation of clinker products.

3.11.1.2. EFFECT OF CLINKER SIZE

After blending, the next step was to produce nodules, it was carried out using mechanical nodule maker. During this process, a range of nodule sizes was produced between 5 mm and 20 mm. To select the critical size for better performance, these nodules were divided into two groups i.e. nodules smaller than 10 mm diameter and bigger than 10 mm diameter as mentioned in Table 3.4. These nodules were clinkered and tested for compressive strength after carbonation. From Fig. 3.5, it can be observed that the effect of clinker size on compressive strength was negligible (less than 2 MPa at an early age and less than 5 MPa after 28-days) for the size range of 5- 20 mm. Therefore, the whole range of clinker sizes was used for further production of cement, this would help to make the production line more energy and time efficient.

3.11.1.3. EFFECT OF CLINKERING TEMPERATURE

The goal of the study was to utilize the MSWI residues and MSW incineration energy to produce eco-cement. The MSW incinerator operates at 1050°C, so to study the effect of clinkering temperature on the quality of eco-cement, the clinkering process was carried out at different temperatures ranging from 1000°C to 1200°C. The performance of the eco-cement produced at different clinkering temperature is presented in Fig. 3.6. It was observed from the results that the compressive strength of the samples was highest when the clinker temperature was 1150°C. However, the strength of cement produced at 1200°C is almost 40% lower than the cement produced at 1150°C. The clinkering temperature of 1100°C is selected for further research because the maximum temperature in the incinerator is 1050°C (Fig. 3.1). It is possible to produce eco-cement in incinerator upper chamber to utilize the incineration energy to make clinkers. The difference in strength between 1000°C and 1100°C was about 6 MPa. The compressive strengths of eco-cement produced at this temperature are comparable with the strength of OPC.

3.11.1.4. EFFECT OF MIXTURE PROPORTIONS

The XRF composition is given in Table 3.1. For the envisioned use of these residues to produce eco-cement, APC residues served as the calcium source and bottom ash with the incorporation of boiler ash served as the silica source. Production of eco-cement at large scale using MSWI residues at 1100 °C clinkering temperature was the major goal of the study. This temperature fit into the production of low temperature or belite-based cements. Based on these limitations, the belite region of the ternary phase diagram was the target region. The mix proportions were decided on the bases of the belite region of C-A-S turnery phase diagram, and based on OPC clinker parameters like LSF, SR, and AR. The two mixes were proposed, and their composition is shown in Table 3.2. The mix composed of 100 % MSWI residues was termed as M1, and the M2 was the mix with the addition of 5.3% of virgin material. The compressive strength and CO_2 uptake of all these proposed mix proportions are presented in Table 3.5. The results showed that eco-cement with the addition of $Ca(OH)_2$ and SiO_2 i.e. M2, had higher carbon reactivity and lower hydraulic behavior, as compared with the mix without additives i.e. M1. Whereas, eco-cement produced entirely from MSWI residues and without any additives showed relatively better hydraulic behavior than the eco-cement with additives. Furthermore, it was observed that the compressive strength of mix with 6 % additives was quite comparable to OPC after carbonation activation. Moreover, the results showed that the raw mix proportions with additives showed higher early strength and lower hydraulic behavior. However, the mix contained 100% MSWI residues showed poor early age carbonation reactivity but good hydraulic behavior after carbonation activation.

Both mixes M1 and M2 showed non-hydraulic behavior, the compressive strength of non-carbonation activated samples was less than 1 MPa. The carbonation activated samples were placed in water to observe the hydration and the stability of eco-cement inside water. It was observed from the 28-day results that the compressive strength of M2 remains almost unchanged, but M1 crossed the 60 MPa mark. It was concluded that eco-cement produced entirely from MSWI-residues showed a non-hydraulic and low-carbonation activation behavior, but after the carbonation curing the hydration mechanism was activated. Moreover, after 28-day immersion of both mixes in the water showed that the developed eco-cements were stable in an aquatic natural exposure condition.

3.11.1.5. EFFECT OF DIFFERENT BATCHES OF RAW MATERIALS

The raw feed of a municipal solid waste incinerator varies season-to-season, even day to day bases over the year in the same municipality. The mineral composition of MSWI residues also changes based on the municipal solid waste fed to the incinerator. Production of the eco-cement with this varying mineral composition of MSWI can be a challenge and a question mark on the practicality of this research program. To tackle this issue, the MSWI ashes were collected during different seasons and random days of a year. The XRF composition of MSWI residues collected from different seasons is presented Table3.6. It was observed from the results, the new binder produced using different MSWI residues collected during different seasons showed consistent compressive strength properties. Moreover, the compression strength results presented in the research are the average of tens of new binder batches produced at different times of the year.

3.12. ANALYSIS OF CLINKERS AND REACTION PRODUCTS

3.12.1. TGA ANALYSIS RESULTS

Thermogravimetric analysis was carried out for both mix batches M1 and M2, OPC paste served as a reference for the study. From Fig. 3.8 and Fig. 3.9(a), it could be observed that the cement paste mass becomes almost constant after 800 °C, which was expected. But almost 10 % mass loss was observed in case of both categories of ecological cement after 800 °C, but still, the drop was continuous, which shows decomposition of some phases which were different than the OPC. The reason for the rapid drop could be the decomposition of the CE phase. Fig. 3.9 shows DTG curves together with TG. In case of carbonated eco-cement pastes (Fig. 3.9(b) and 3.9(c)), there was a continuous mass loss over the entire range of test temperature (i.e., from 23°C to 1000 °C). The largest mass loss was observed in the temperature range from about 500°C to 700°C. The mass loss in the temperature region of 500°C to 700°C is attributed to the decomposition of $CaCO_3$. The mass loss at the temperature of 100°C indicated the loss of both, physically and chemically bound water present in the gel phases.

3.12.2. QXRD RESULTS

Table 3.7 summarizes the mineral phases in as-produced eco-cement and carbonated eco-cement paste detected by a quantitative XRD technique. Chlorellestadite (CE) with the chemical formula $Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$ was identified as a major phase, which was a new phase in a cement binder. The analysis was performed for two materials: (1) Eco-cement; and (2) Eco-cement paste after two hours of carbonation. Both batches of M1 and M2 were analyzed. The QXRD studies showed the presences of a new phase chlorellestadite (CE). This phase was not the target clinker phase, but due to the complex composition of raw feed made the formation of this phase possible. Literature explained that the Ellestadite belongs to the silicate sulfate apatite group of minerals, with variants distinguished by their end-members: OH (hydroxyl-ellestadite), F (Fluor-ellestadite), and Cl (chlorellestadite) [19]. The raw feed of the eco-cement is very rich in Ca, Si, S, and Cl, and the raw clinker blend fit the compositional requisite for CE formation. Since clinkering was performed at 1100°C, which is most likely crystallization temperature associated with the formation of this phase. The CE was reduced by 50% during the carbonation activation of both batches i.e. M1 and M2. The other carbon reacted phase was larnite, which is a β- polymorph of belite, which was expected. The clinkering temperature of 1100°C is rational for belite production. The belite reacted with CO_2 and produced $CaCO_3$ and C-S-H (Equation. 3.1). The reduction in CE seemed to be connected with the formation of gypsum. The QXRD results strongly suggested that the binding matric produced in carbonation cured eco-cements comprised of C-S-H or a modified C-S-H and $CaCO_3$, but also included a gypsum component. These reductions in CE and belite after the carbonation curing were equally met with an increase in the contents of vaterite, gypsum, and the amorphous phase. Furthermore, the amount of CE was observed higher in M1 as compared to M2, it was expected as M1 was produced entirely from the MSWI residues. The quantities of gypsum and vaterite were lesser in the carbonation cured M1, which showed the reaction deficiency of M1 and ultimately resulted in the low initial strength. Moreover, the presence of non-CO_2-reactive phases within the clinkers were also found during the scan, namely, wadalite, and Bredigite. A couple of phases reacted in a very minor or negligible amount such as Halite and Sylvite. These were seemingly unaffected by carbonation as their proportions in the clinkers and carbonated specimens were relatively unchanged.

3.12.3. SEM RESULTS

Microstructural studies were carried out after the carbonation curing of eco-cement pastes. The micrographs of carbonation cured samples are presented in Fig. 3.10. The morphology of M1 showed physical porosity, the crystals observed were not fully grown, and density and cohesion of the of crystals were also not observed. In contrary, a micrograph of M2 showed well-defined microstructure quite comparable to the OPC. The density and compactness of M2 and OPC crystals could be compared, but the shapes are different which needs more detailed investigation. Furthermore, the morphology of M2 showed denser microstructure and fewer spaces in between the crystals as compared to M1. The well-grown, compact, denser and less spaces in between the crystal structure could have contributed to the high early strength of M2.

EDS analysis was performed to observe the elemental composition of carbonation cured eco-cement paste phases. The EDS of carbonation cured M1 and M2 are presented in Fig. 3.11. Un-reacted hexagonal CE crystals were observed in M1 micrographs and EDS confirmed the all essential element of EDS (spot "C"). The amorphous like phases were also observed, the presence of high amounts of Ca, Si, and oxides with some amount of chlorine and carbon pointed toward the formation of amorphous calcium silicate hydrocarbonate modified (A-C-S-H), it can be observed in spot "A". The new phase identified was believed to be a modified calcium silicate hydrate (C-S-H), which is alleged to be the binding and strength contributing phase of OPC. The modified phase of gypsum was also identified during the EDS analysis of M1 and can be observed in spot "A" of Fig.3.11(a). in addition, modified amorphous calcium silicate hyrdrocarobante was also detected in M2, and it can be observed from the spot "A" of Fig. 3.11(b). The presence of the A-C-S-H in M2 strengthened the notion of an increase in amorphous phase found in the QXRD analysis. The calcium carbonate phases were also observed from the EDS and sodium chloride was also detected in carbonation cured eco-cement pastes, these phases can be observed in the spot "D" and spot "C" respectively.

3.13. LEACHING PERFORMANCE

Table 3.8 summarizes the leaching performance of the raw blend, eco-cement after clinkering and pulverizing, and carbonated eco-cement. The EPA test methods were adopted to simulate exposure conditions that varied in severity. It was observed that all the heavy metal concentrations measured in the respective leachates were well below regulatory limits defined by EPA. However, a couple of interesting facts were observed; firstly, Pb was present in a quite significant amount, but after clinkering the Pb leaching amounts were dropped well within the EPA limits, the Pb may have been incorporated in the clinker phases during the clinkering process that occurred at elevated temperature and was effectively stabilized. Furthermore, leaching of chromium (Cr) was increased after the clinkering, it showed that the Cr was released from the binding compounds during the clinkering. This leachable Cr was get fixed into new reactive phases after the carbonation and it was immobilized to the limiting value of 5mg/l. These findings were in a good agreement to the past research, except the Cr immobilization after carbonation [20-22]. Carbonation activation helped the stabilization process by contributing in two ways. Firstly, carbonation activation densified the hardened matrix by the precipitation of micro-sized $CaCO_3$, the overall porosity and permeability were reduced, this helped to reduced leaching physically. Secondly, the biding of hazardous materials within the reaction product as per the principal of cement stabilization of waste [23].

There were three processes that have contributed to the stability of CO_2-activated clinker; (1) Thermal stabilization, which took place during the clinkering process and destroyed the organic contamination found and structurally bound the Chlorine and Sulfur into the clinker phases such as CE. (2) Accelerated carbonation contributed in the stabilization by physical bounding of the hazardous material in the binding matrix and (3) densification of the hardened matrix which reduced the porosity and permeability of the microstructure. This reduction in porosity and permeability ultimately helped in the withholding of the leachable.

3.14. ECO-CONCRETE BLOCKS

The ultimate goal of this research is to produce commercial product i.e. concrete masonry blocks. The target strength of eco-concrete bricks depends on applications. The minimum strength for concrete blocks can vary from 18 to 25 MPa (CSA A 165.2-14). As an initial trial, 50 x 50 x 25 mm eco-concrete slabs were produced using ecological cement and compared with the OPC concrete slabs. Concrete bricks were produced using 15 % of cement loading, w/c ratio of 35 %, fine aggregate by 48 % and coarse aggregate by 32 %. The maximum size of the coarse aggregate was 10 mm. The mix design remains the same only the OPC was replaced with eco-cement. It can be seen from Fig. 3.12, the strength of eco-concrete is quite comparable to OPC concrete, and most importantly the ecological cement could be used to produce concrete blocks.

3.15. CONCLUSIONS & SUMMARY

i. A green low-energy ecological cement can be derived exclusively from municipal solid waste incineration residues, with the potential of sequestering CO_2 and conserving natural resources. This ecological cement will contribute towards environmental sustainability by utilizing the MSW incineration residues, reducing the landfill of waste material, reducing the carbon emission from MSW incineration, and converting wastes into value-added products.

ii. Cement can be produced at a different clinkering temperature ranging from 1000°C to 1300°C, but 1100°C is the optimum temperature in terms of conservation of energy, economy, and strength. Cement produced entirely from MSWI residues was more hydraulic than the cement produced using some 6 % of pure calcium oxide and silica oxide. Chlorellestadite was the major clinker phase identified in the binder. This phase fixed the Chlorine and Sulphur in its composition and it showed CO_2 reactivity. Stabilization of the binder seemed to be the result of a combined effect of the mechanisms of clinkering, binding-matrix generation, and carbonate precipitation.

iii. Cement paste strength of the new binder after 2-hours of CO_2 curing was comparable to the 28-days hydrated paste of the OPC. Furthermore, the practical use of the binder in concrete was demonstrated by using granite aggregate, ecological cement concrete showed almost equal strength to the OPC concrete; Moreover, this strength was also higher than the concrete brick strength requirements of CSA-A165.

iv. Finally, the goal is to convert the incineration facility into a cement production plant by utilizing the waste ashes generated as a raw meal for cement production, the heat energy produced during burning of waste material for clinkering and emitted CO_2 will be utilized to cure/ activate the binder. Moreover, the consistency in the performance of the new binder produced using MSWI ashes from different seasons over the year emphasized the practicality of this study.

REFERENCES

1. Aubert, J.E., B. Husson, and A. Vaquier, *Use of municipal solid waste incineration fly ash in concrete*. Cement and Concrete Research, 2004. **34**(6): p. 957-963.
2. Canada, S. *Waste Management Industry Survey*. [Online] 2006 [cited 2018 August 20, 2018]; Available from: https://www150.statcan.gc.ca/n1/pub/16f0023x/16f0023x2013001-eng.htm.
3. Wiles, C.C., *Municipal solid waste combustion ash: State-of-the-knowledge*. Journal of Hazardous Materials, 1996. **47**(1): p. 325-344.
4. Ampadu, K.O. and K. Torii, *Characterization of eco-cement pastes and mortars produced from incinerated ashes*. Cement and Concrete Research, 2001. **31**(3): p. 431-436.
5. Kikuchi, R., *Recycling of municipal solid waste for cement production: pilot-scale test for transforming incineration ash of solid waste into cement clinker*. Resources, Conservation and Recycling, 2001. **31**(2): p. 137-147.
6. Lee, T.-C., W.-J. Wang, P.-Y. Shih, and K.-L. Lin, *Enhancement in early strengths of slag-cement mortars by adjusting basicity of the slag prepared from fly-ash of MSWI*. Cement and Concrete Research, 2009. **39**(8): p. 651-658.
7. Siddique, R., *Utilization of municipal solid waste (MSW) ash in cement and mortar*. Resources, Conservation and Recycling, 2010. **54**(12): p. 1037-1047.
8. Mindess, S., *Concrete*. 2nd ed. 2002: Prentice Hall. 644.
9. Odler, I., *Special Inorganic Cements*. 2000: CRC Press.
10. Bukowski, J.M. and R.L. Berger, *Reactivity and strength development of CO<inf>2</inf> activated non-hydraulic calcium silicates*. Cement and Concrete Research, 1979. **9**(1): p. 57-68.
11. Young, J.F., R.L. Berger, and J. Breese, *Accelerated Curing of Compacted Calcium Silicate Mortars on Exposure to CO2*. Journal of the American Ceramic Society, 1974. **57**(9): p. 394-397.

12. El-Hassan, H., Y. Shao, and Z. Ghouleh, *Effect of Initial Curing on Carbonation of Lightweight Concrete Masonry Units*. Vol. 110. 2013. 441-450.

13. Rostami, V., Y. Shao, and A.J. Boyd, *Durability of concrete pipes subjected to combined steam and carbonation curing.* Construction and Building Materials, 2011. **25**(8): p. 3345-3355.

14. Lange, L.C., C.D. Hills, and A.B. Poole, *The influence of mix parameters and binder choice on the carbonation of cement solidified wastes.* Waste Management, 1996. **16**(8): p. 749-756.

15. Gunning, P., C. Hills, and P. Carey, *Production of lightweight aggregate from industrial waste and carbon dioxide*. Vol. 29. 2009. 2722-8.

16. Shi, H.S. and L.L. Kan, *Leaching behavior of heavy metals from municipal solid wastes incineration (MSWI) fly ash used in concrete.* J Hazard Mater, 2009. **164**(2-3): p. 750-4.

17. Fernandez Bertos, M., S.J. Simons, C.D. Hills, and P.J. Carey, *A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2.* J Hazard Mater, 2004. **112**(3): p. 193-205.

18. Guo, X., H. Shi, K. Wu, Z. Ju, and W.A. Dick, *Performance and risk assessment of alinite cement-based materials from municipal solid waste incineration fly ash (MSWIFA).* Materials and Structures, 2015. **49**(6): p. 2383-2391.

19. Rouse, R.C. and P.J. Dunn, *A contribution to the crystal chemistry of ellestadite and the silicate sulfate apatites*. Vol. 67. 1982. 90-96.

20. Baciocchi, R., G. Costa, E. Di Bartolomeo, A. Polettini, and R. Pomi, *The effects of accelerated carbonation on CO2 uptake and metal release from incineration APC residues.* Waste Management, 2009. **29**(12): p. 2994-3003.

21. Wieser, T. and H. Weigand, *Stabilization of Heavy Metals in MSWI Bottom Ash by Enhanced Carbonation*. 2014.

22. Ghouleh, Z. and Y. Shao, *Turning municipal solid waste incineration into a cleaner cement production.* Journal of Cleaner Production, 2018. **195**: p. 268-279.

23. Batchelor, B., *Overview of waste stabilization with cement.* Waste Management, 2006. **26**(7): p. 689-698.

Table 3.1: Chemical compositions of MSWI ashes and OPC

Compounds	APC Lime %	Boiler Ash %	Bottom Ash %	OPC %
CaO	55.47	18.31	12.71	63.53
SiO_2	1.79	10.05	25.91	21.64
Al_2O_3	0.17	4.1	10.57	4.42
Fe_2O_3	0.15	2.19	4.81	2.79
TiO_2	0.09	1.69	2.17	0.27
MnO	0.01	0.07	0.44	0.06
MgO	1.06	1.57	1.81	2.79
Na_2O	0.41	8.83	2.09	DL
K_2O	0.49	6.52	1.16	0.55
P_2O_5	0.13	1.4	1.44	0.25
Cl	17.3	6.21	1.59	--
S-total	0.43	10.9	0.6	1.60
C-total	1.97	0.02	23.7	0.32
LOI	18.37	0.02	23.7	0.52

Table 3.2: Mixture proportion and calculated process parameters

Mix	APC %	Boiler Ash %	Bottom Ash %	Added Ca(OH)2 %	Added SiO2 %	LSF	SR	AR
M1	45.00	30.00	25.00	0.00	0.00	0.97	1.75	2.05
M2	36.04	28.80	28.80	4.90	1.47	0.87	1.73	2.07

Table 3.3: Different blending methods

Mix	Blending method
Blend 1	Blend by mortar mixer
Blend 2	Blend by rotating ball mill
Blend 3	Blend by a turn-over rotating ball mill

Table 3.4: Different clinker sizes

Mix	Mixing method
Clinker 1	Clinker sizes smaller than 10 mm sieve produced by blending in rotating ball mill mixer
Clinker 2	Clinker sizes larger than 10 mm sieve produced by mixing in rotating ball mill mixer
Clinker 3	Clinker sizes smaller than 10 mm sieve produced by blending in turn-over ball mill mixer
Clinker 4	Clinker sizes larger than 10 mm sieve produced by mixing in turn-over ball mill mixer

Table 3.5: Compressive strength and CO2 uptake after 2h carbonation

Mix	Carbon uptake (%)	Avg. Strength (MPa)			
		Control (2h)	2 hours	7 Days	28 Days
M1	3.33	3.20	16.67	26.70	55.20
M2	7.80	1.00	53.20	54.50	55.00

Table 3.6: Chemical compositions of MSWI ashes collected during different seasons

Compounds	**Season 1**			**Season 2**		
	APC Lime	**Boiler Ash**	**Bottom Ash**	**APC Lime**	**Boiler Ash**	**Bottom Ash**
	%	**%**	**%**	**%**	**%**	**%**
CaO	55.47	18.31	12.71	41.11	20.31	14.78
SiO_2	1.79	10.05	25.91	1.79	18.28	18.88
Al_2O_3	0.17	4.1	10.57	1.43	14.47	9.55
Fe_2O_3	0.15	2.19	4.81	0.42	2.30	4.64
TiO_2	0.09	1.69	2.17	0.03	1.76	1.87
MnO	0.01	0.07	0.44	0.03	0.09	0.095
MgO	1.06	1.57	1.81	4.86	6.73	1.75
Na_2O	0.41	8.83	2.09	0.91	12.66	1.53
K_2O	0.49	6.52	1.16	0.20	2.21	0.88
P_2O_5	0.13	1.4	1.44	0.26	3.50	1.46
Cl	17.3	6.21	1.59	5.85	3.54	1.23
S-total	0.43	10.9	0.6	0.75	10.95	0.6
C-total	1.97	0.02	23.7	4.06	2.09	25.7
LOI	18.37	0.02	23.7	16.48	18.37	41.45

Table 3.7: Quantitative phase analysis of as-synthesized and after 2h carbonation activation via QXRD for Clinker at 1100°C

Mineral	**Compound**	**Mix M2**		**Mix M1**	
		Eco-cement (%)	**carbonated eco-cement (%)**	**Eco-cement (%)**	**carbonated eco-cement (%)**
Chlorellestadite	$Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$	43.8	21.6	49.8	27.8
Wadalite	$Ca_6Al_5Si_2O_{16}C_{l3}$	9.4	9.4	9.8	10.0
Bredigite	$Ca_7Mg(SiO_4)_4$	8.0	8.0	3.8	3.5
Belite	Ca_2SiO_4	9.3	4.5	13	10.3
Quartz	SiO2	0.5	n.d	0.4	n.d
Halite	NaCl	4.9	4.7	5.1	4.9
Sylvite	KCl	2.4	1.9	2.0	1.9
Gypsum	CaSO4.2(H2O)	n.d.	6.2	n.d	3.3
Vaterite	CaCO3	n.d.	4.5	n.d	2.3
X-Ray insensitive	Amorphous	21.8	39.3	16.1	36.2

Table 3.8: TCLP results comparing leaching behavior of the raw clinker blend to its heat-treated form, both before and after carbonation.

Compounds/elements	Units	Raw Mix	Eco-cement	Carbonation Activated	Detection Element	Regulatory Limits
Arsenic (As)	mg/L	<0.050	<0.050	0.187	0.05	5
Barium (Ba)	mg/L	1.19	0.7	0.52	0.5	100
Cadmium (Cd)	mg/L	<0.0050	<0.0050	0.0084	0.005	1
Chromium (Cr)	mg/L	<0.050	14.1	4.85	4.95	5
Lead (Pb)	mg/L	13.4	<0.050	<0.050	0.05	5
Mercury (Hg)	mg/L	<0.00010	<0.00010	<0.00010	0.0001	0.2
Selenium (Se)	mg/L	<0.025	<0.025	<0.025	0.025	1
Silver (Ag)	mg/L	<0.0050	<0.0050	<0.0050	0.005	5

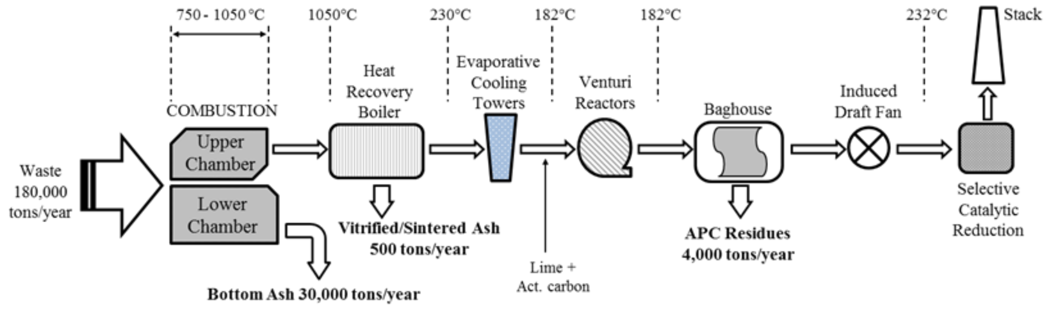


FIGURE 3.1: PROCESS FLOW DIAGRAM OF MSW INCINERATION AT EMERALD EFW PLANT

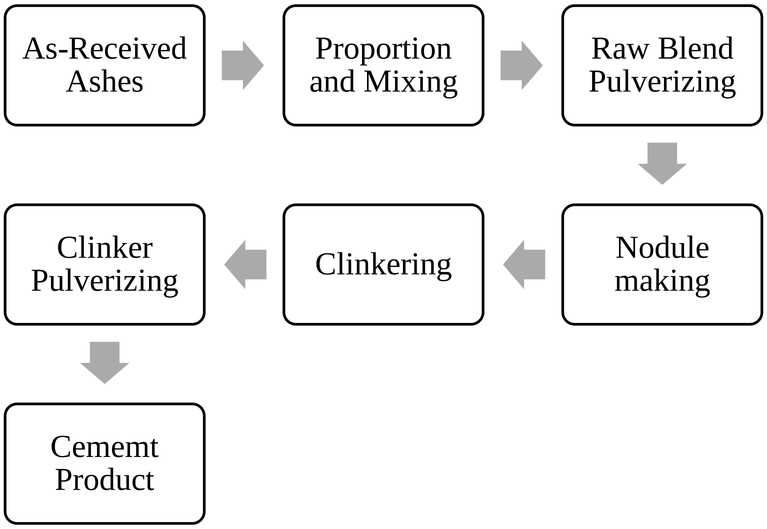


FIGURE 3.2: FLOW CHART OF CEMENT PRODUCTION FROM MSWI ASHES

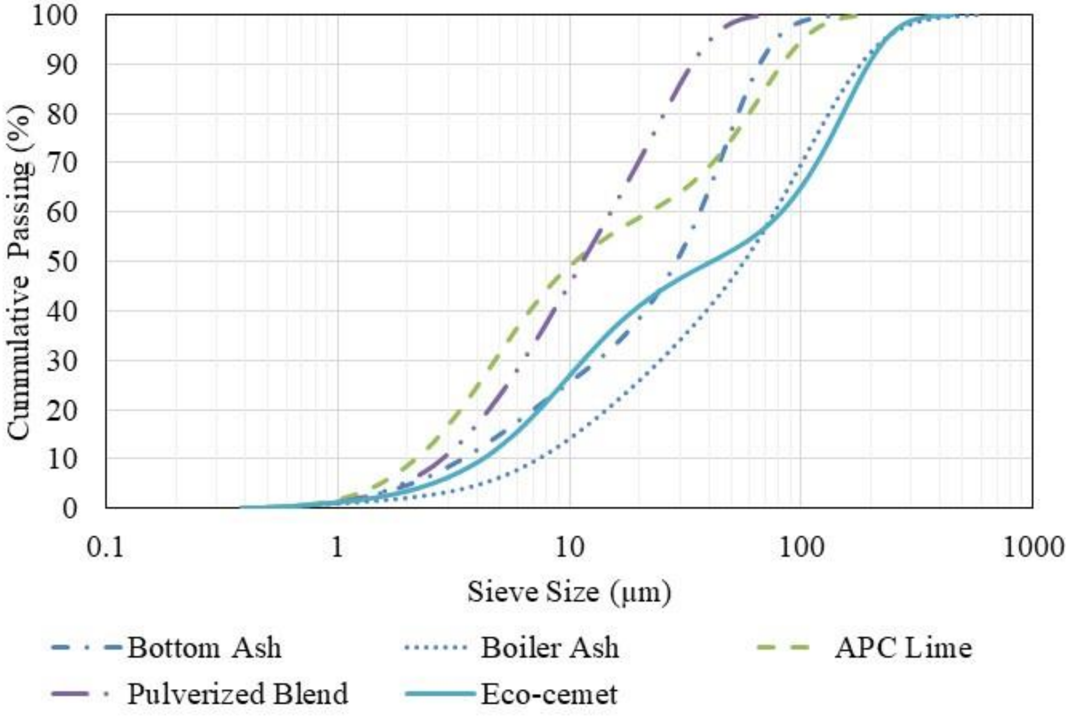


FIGURE 3.3: SIEVE ANALYSIS OF AS-RECEIVED MSWI RESIDUES, PULVERIZED BLEND, AND ECO-CEMENT

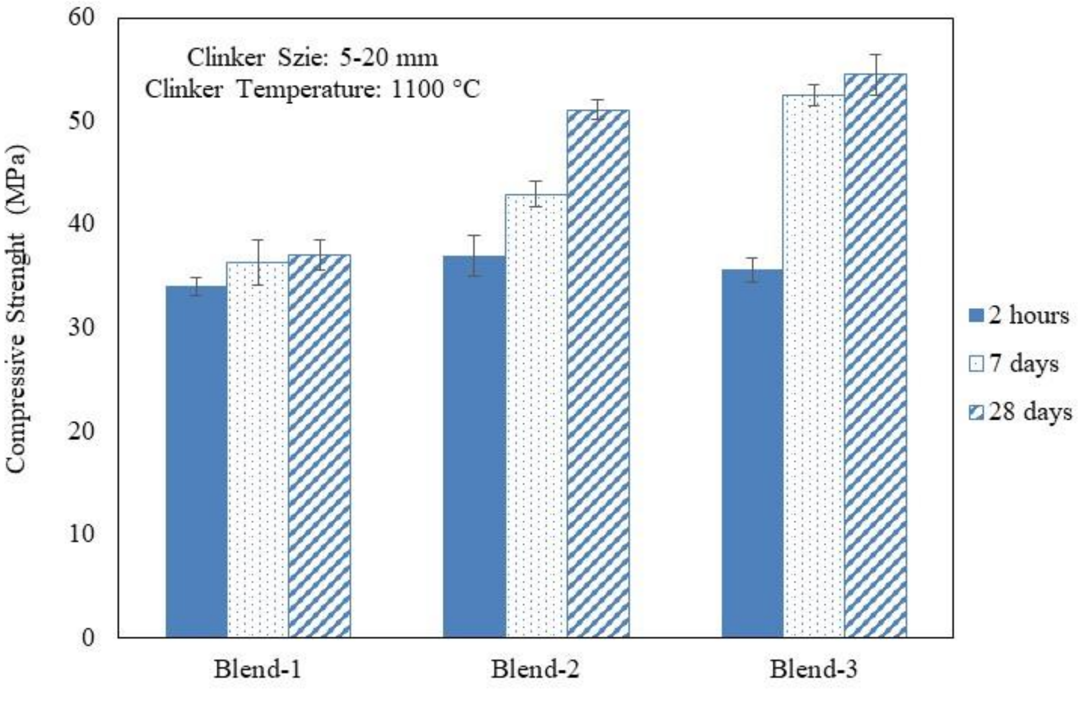


FIGURE 3.4: EFFECT OF RAW MATERIAL BLENDING ON COMPRESSIVE STRENGTH

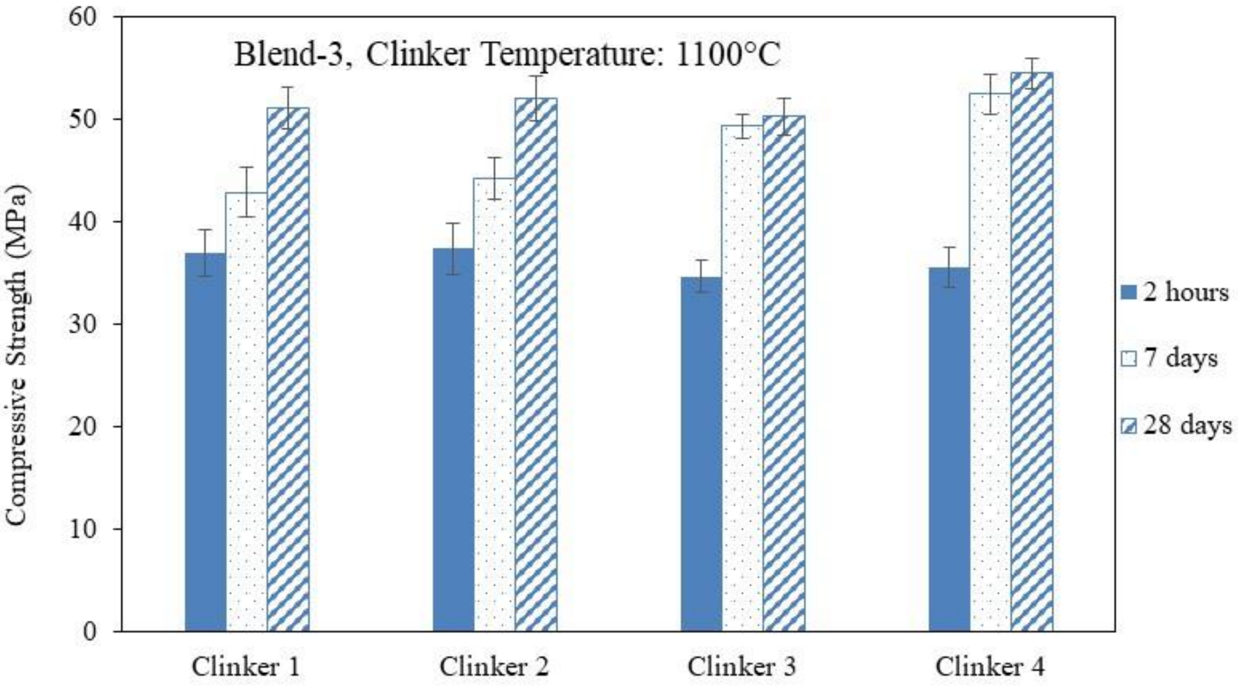


FIGURE 3.5: EFFECT OF CLINKER SIZE ON COMPRESSIVE STRENGTH

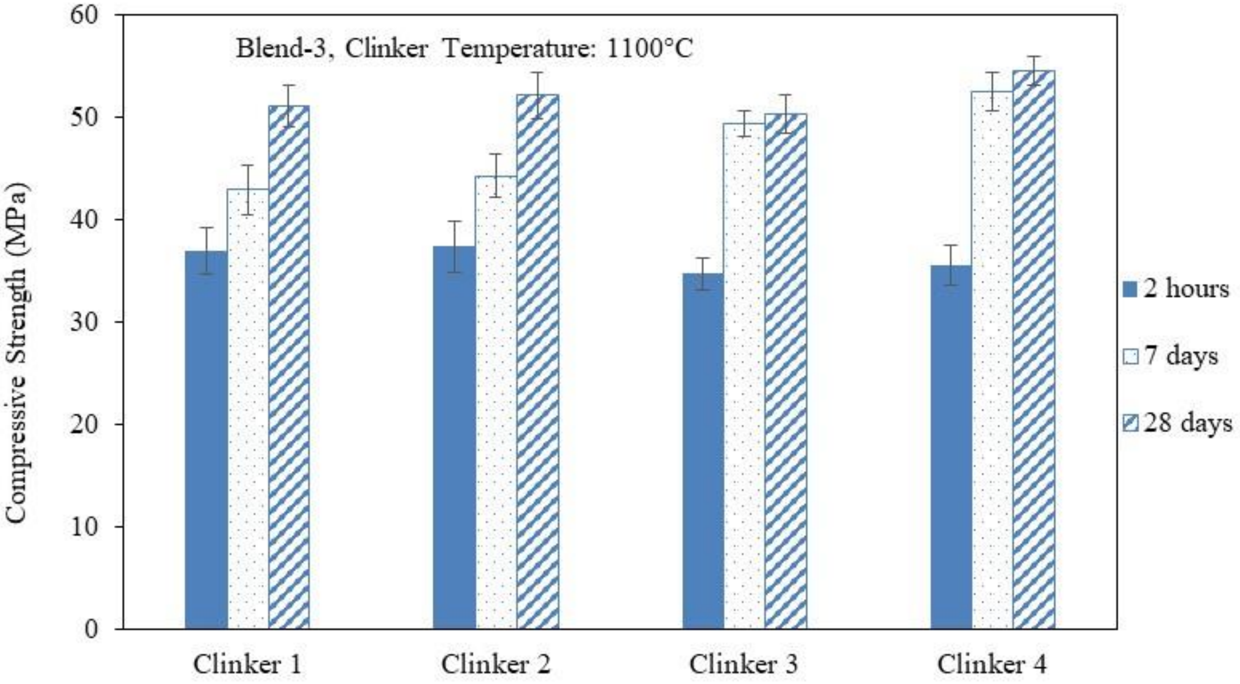


FIGURE 3.6: EFFECT OF CLINKERING TEMPERATURE ON THE COMPRESSIVE STRENGTH OF CEMENT AFTER 2H CARBONATION

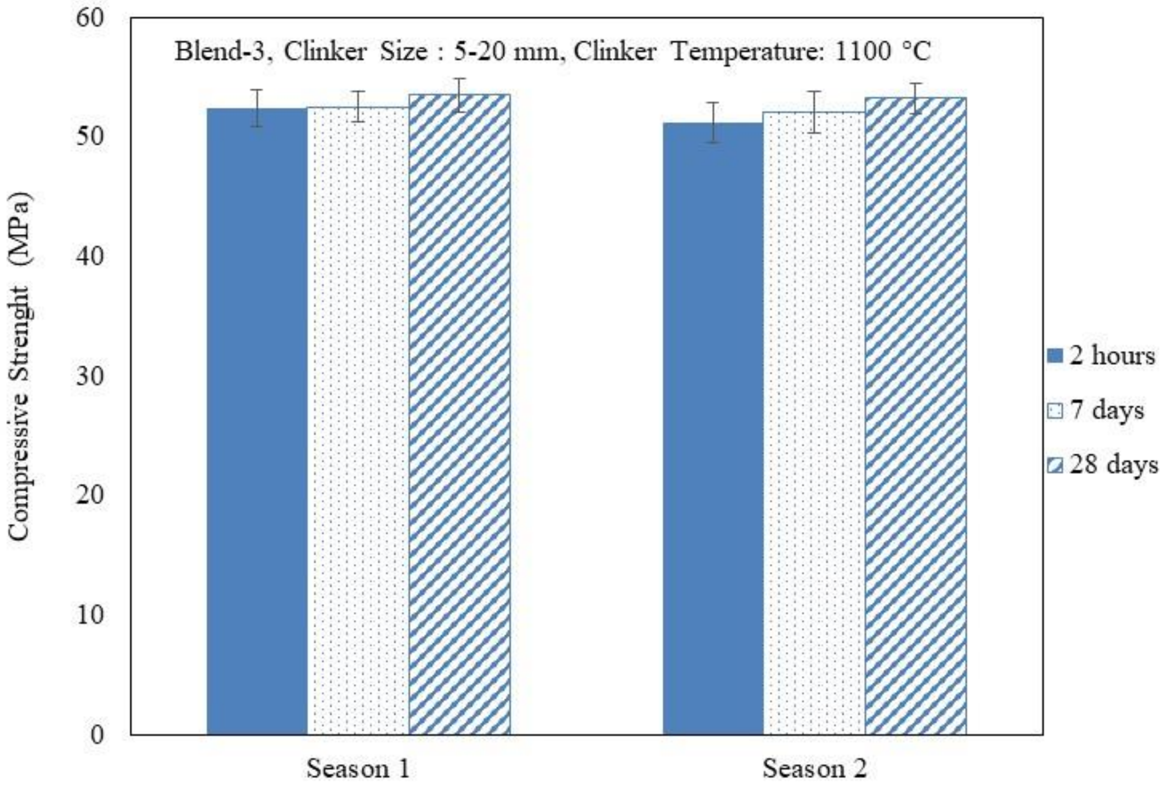


FIGURE 3.7: EFFECT OF VARIATIONS OF RAW MATERIALS ON COMPRESSIVE STRENGTH

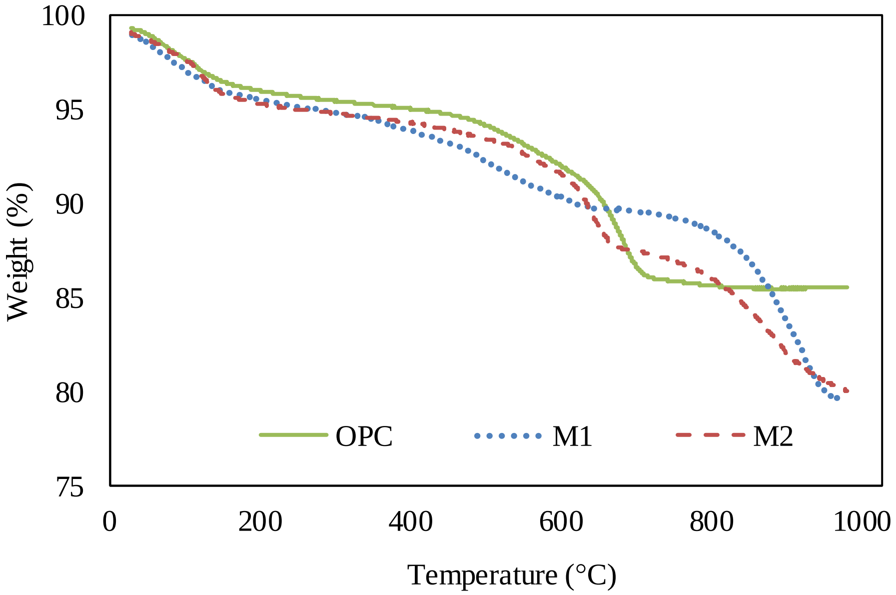
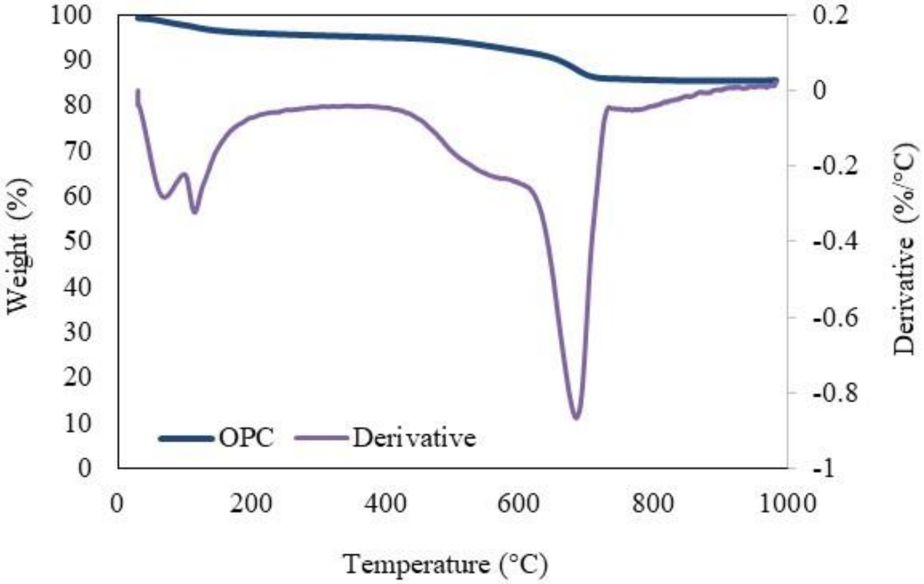
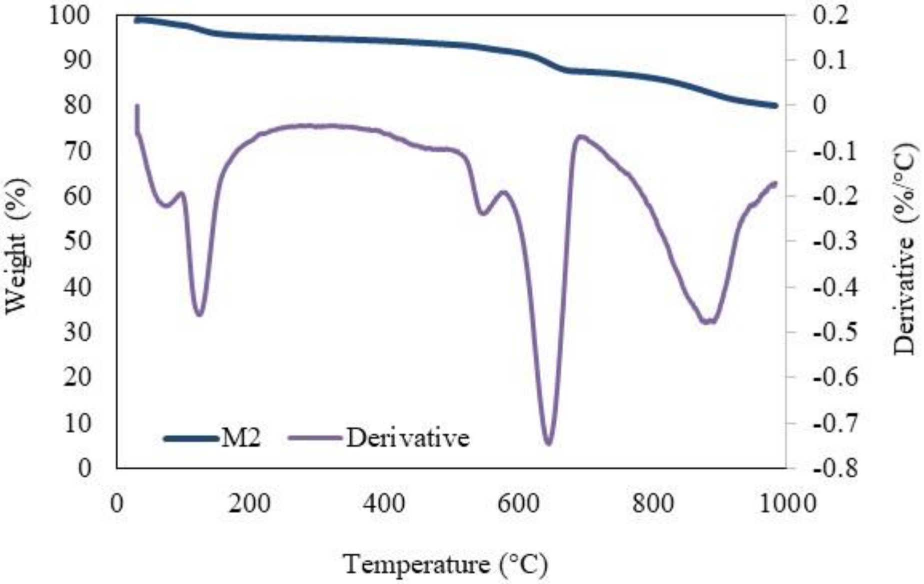


FIGURE 3.8: TGA CURVES OF M1, M2, AND OPC PASTE AFTER CARBONATION CURING



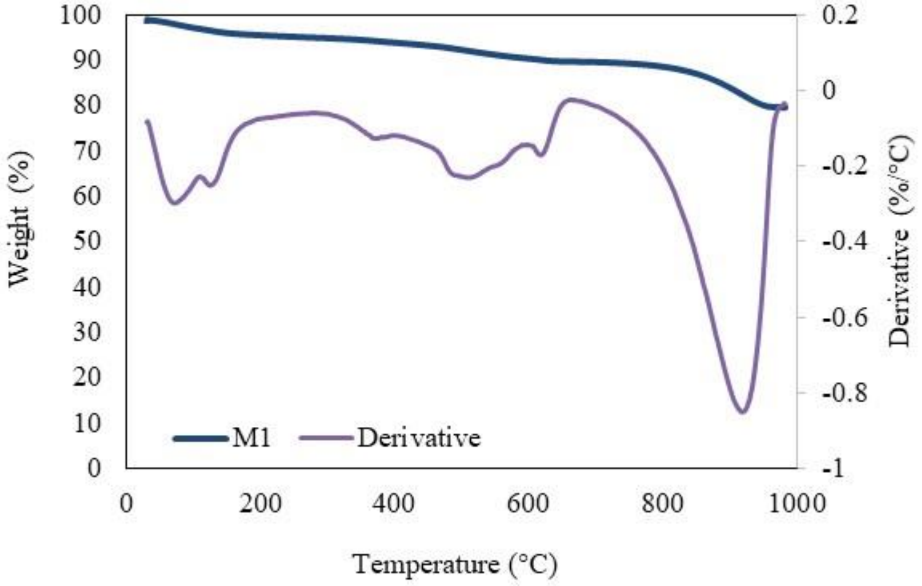
100
90
80
70
60
50
40
30
20
10
0
Weight (%)
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
Derivative (%/°C)
0
200
400
600
800
1000
Temperature (°C)
OPC
Derivative

(a)



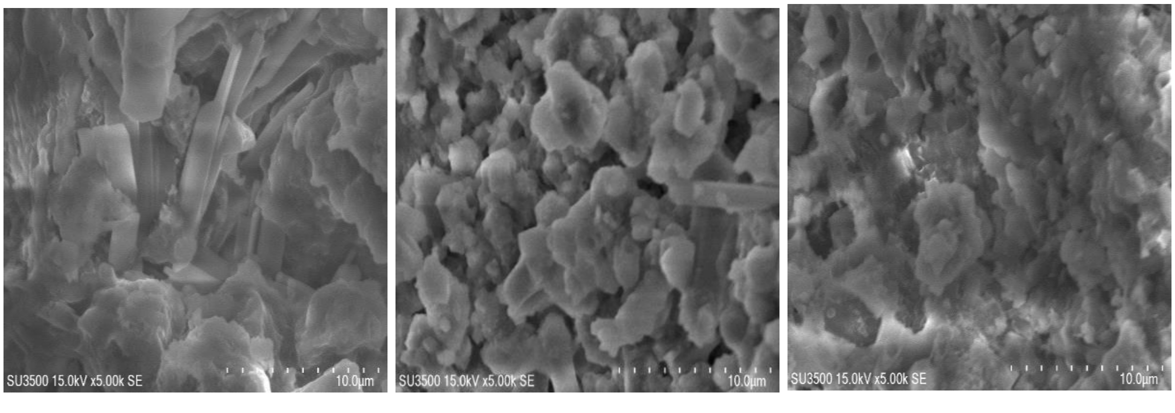
100
90
80
70
60
50
40
30
20
10
0
Weight (%)
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
Derivative (%/°C)
0
200
400
600
800
1000
Temperature (°C)
M2
Derivative

(b)



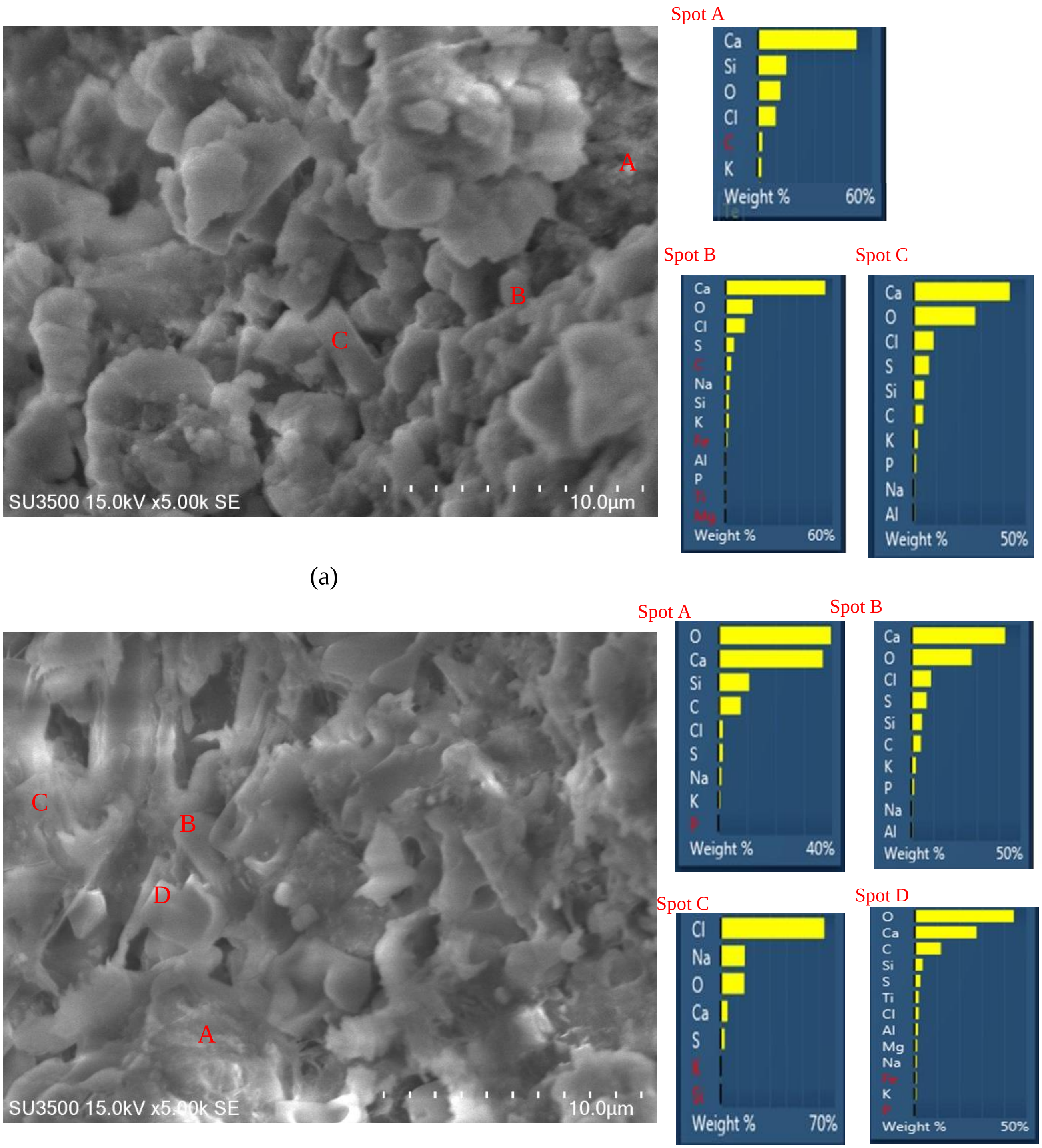
(c)

FIGURE 3.9: TGA+DTG CURVES AFTER 2 HOURS OF CARBONATION CURING (A): OPC PASTE (B): M1 PASTE (C): M2 PASTE



(a) (b) (c)

FIGURE 3.10: SEM MICROGRAPHS OF CEMENT PASTE AFTER 2 HOURS OF CARBONATION (A):OPC PASTE (B): M1 PASTE (C):M2 PASTE



(a)

(b)

Figure 3.11: EDS analysis of cement paste after 2-hours of carbonation (a): EDS analysis of M1 paste (b): EDS analysis of M2 paste

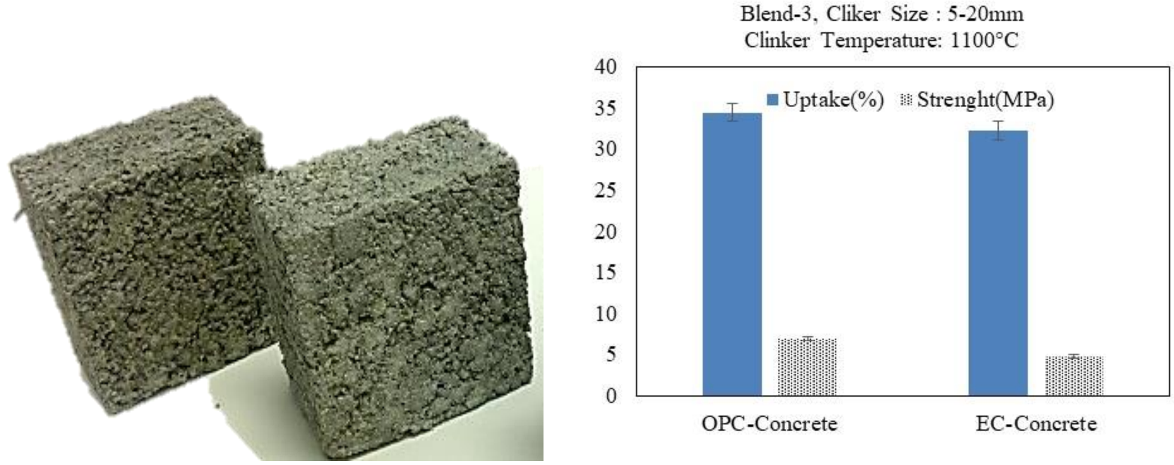


Figure 3.12: Eco-Concrete bricks compressive strength results

CHAPTER 4. CHARACTERIZATION OF ECO-CEMENT MADE FROM MUNICIPAL SOLID WASTE INCINERATION RESIDUES

PREFACE

Production of eco-cement from the municipal solid waste incineration residues was discussed comprehensively in Chapter 3. Eco-Cement achieved an average strength of 55 MPa after two hours of accelerated carbonation reaction which is comparable to the average strength of Ordinary Portland Cement (OPC). It is sustainable and environmentally friendly as it is derived from the waste residues, produced with incineration energy, and will serve as a potential carbon sink. Nevertheless, the microstructure of eco-cement formed by carbonation is expected to be noticeably different from that of the hydration of conventional OPC. Thus, understanding of microstructure formed after carbonation is essential. This chapter is envisioned for an in-depth study of the microstructure formed after two hours and twelve hours of accelerated carbonation, and a better understanding of swift strength development mechanism.

The objective of this chapter is to study the composition and the microstructure of the eco-cement and eco-cement paste after the carbonation activation. This study will help to understand the rapid strength mechanism after two hours of carbon activation. Furthermore, it will also help to understand the secondary reactions taking place after the twelve hours of accelerated carbonation which results in a 50 % strength increment.

4.1. ABSTRACT

Non-hydraulic eco-cement made from Municipal Solid Waste Incineration residues can gain strength upon carbonation activation. The compressive strength of the eco-cement after two hours of carbonation activation could reach 55 MPa which was quite comparable to the ordinary Portland cement. In this chapter, the effect of carbonation time on strength gain is presented. It was found that a compressive strength of 80 MPa could be obtained after twelve hours of carbonation activation. The mechanism of the strength gain from carbonated eco-cement was also studied. Quantitative X-Ray Diffraction (QXRD) analysis showed primary active components were chlorellestadite (CE) and larnite, with an increase in the amorphous phase. It was observed that carbonation of CE and larnite produced the calcium carbonates, complex phase of calcium silicates hydrocarbonate, and gypsum. The microscopic evaluation also revealed the presence of complex calcium silicate phases (an amorphous or very low crystalline phase). Thermogravimetric Analysis (TGA) and Fourier-Transform Infrared (FTIR) spectroscopy also demonstrated the presence of calcium carbonates and polymerization of calcium silicates present in the form of larnite and CE.

Keywords: Eco-cement, MSWI residues, accelerated carbonation, chlorellestadite, belite

4.2. INTRODUCTION

Municipal Solid Waste (MSW) production is estimated about 1 to 2 billion tons per year worldwide [1]. MSW is either disposed of in a landfill or incinerated. Incineration reduces the volume and the mass of waste, and energy is produced during the incineration process because of its high calorific values. The areas where the population densities are moderately high, and the landfill sites are limited, the incineration of MSW is the desirable choice [2]. The incineration of MSW results into three by-products namely bottom ash, fly ash and air pollution control (APC) residues; APC residues contain large amounts of chlorides, heavy metals, and organic contaminations [3, 4]. Contrary to this, the boiler ash and APC lime are very rich in silica and lime, which could be used as a raw meal for cement production [3, 5]. The organic contaminations (dioxins, furans) can effectively be destroyed and heavy metals can be fixed within clinker phases during the cement production process at elevated temperatures [5, 6]. Many researchers effectively used the MSW incineration (MSWI) residues to produce environmentally friendly cements. Most of the researchers used MSWI residues from 20-60 % of the raw feed and the clinkering temperature was varied between 1100 °C to 1400 °C to produce cements [5, 7-9]. Zaid and Shao have successfully produced a carbonation activated cement binder using 85 % of MSWI residues at 1000°C. The cement binder showed no hydraulic reactivity, but it achieved compressive strength of over 50 MPa with a carbon dioxide uptake capacity of about 7% [10]. In Chapter 3 of this thesis, an eco-cement was successfully produced using all the MSWI residues i.e. bottom ash, boiler ash, and APC lime, up to 95 % of the raw feed, and the clinkering was carried out at 1100°C. The compressive strength and CO_2 uptake were achieved to be more than 55 MPa and 6 % respectively. It was observed from the QXRD analysis of the eco-cement that the major reactive phases were chloroellestadite (CE) and larnite. Ellestadite is a part of apatite group of silicate sulfate minerals, it could be found and with different end members and term on the same end member: Cl (chloro-ellestadite), F (Fluor-ellestadite), and OH (hydroxyl-ellestadite). Through the lattice substitution, Apatites can structurally accommodate different atoms [11]. Waste incineration residues could have the bulk of different types of contaminations; especially chlorides, heavy metals, and sulfates, CE could be a promising host material for all these containments [11]. The MSWI residues are rich in Si, Ca, Cl and S, the CE formation during clinkering is understandable. The temperature ranges from 900°C to 1200°C is very auspicious for the CE production, and the 1100°C is the peak crystallization temperature for this phase [10, 12]. CE is a water-insoluble compound, and it showed non-hydraulic behavior, but interestingly it showed very high carbon reactivity [10, 12]. When CE based eco-cement, the paste was exposed to the accelerated carbonation curing, CE reacts with CO_2 and contributed to the increase of $CaCO_3$ and gypsum formation.

On the other hand, Belite based cements are being considered more sustainable as compared to the OPC, because these cements are produced at a lower temperature and emit lesser CO_2 [13]. It is well-established fact that concrete is the second most consumed material in the world in terms of the total volume of the material, obviously, water is on the top of the most consumed material around the world [14]. In 2016, more than 4.2 billion metric tons of cement was produced, and this amount is projected to increase by 2.5 % annually [15, 16]. Cement is a very energy intensive and its production requires very large quantities of natural resource i.e. each ton of cement production requires more than 1.6 ton of natural resources, which are limited on planet earth. Burning of the fossil fuels to fulfill the energy required to produce cement and calcination of limestone emits very high amount CO_2, a ton of CO_2 is emitted during the production of each tone of cement. That is why the cement industry is one of the largest sources of CO_2 emission, the cement industry emits about 5 % of total CO_2 emissions [17]. Accordingly, one of the major challenges for the concrete and cement industry is to find the alternative binding cementitious system with lower carbon emissions as compared to the OPC. The carbon footprint could be reduced by multiple means i.e. by using alternative fuels, use of supplementary cementitious materials, carbon capture and storage, and production of alternative cements. There are many alternative cementitious systems with lower carbon footprint has been reported during the last decade [18]. Low-hydraulic to non-hydraulic calcium-silicate cements are one of the most recent additions to the low-carbon footprint alternative clinker systems [19]. These binders are composed of wollastonite ($CaO.SiO_2$) and rankinite ($3CaO.2SiO_2$) i.e. low-lime calcium silicates [20]. These cements are produced at lower energies and the major component is belite as compared to the OPC having alite as a major component. Due to the lack of hydraulic reactivity of belite as compare to the alite, it has been considered as undesirable components of OPC. On the other hand, the belite was found to exhibit enhanced reactivity in the presence of CO_2 [21, 22,23]. The production temperature of these cement binders is about 200-300°C lesser than the OPC, as these cement binders are produced at 1200-1250°C. As mentioned earlier, the hardening and strength generation of these low-temperature cement binding cements and cement phases (includes belite rich cement, calcium-silicate cements, γ- polymorph of belite, β-C_2S, rankinite, wollastonite, pseudowollastonite, etc.) requires accelerated carbonation, and the strength of these systems is equal to the 28 days hydrated strength of OPC [13, 24]. When subjected to accelerated carbonation, these binder systems can store CO_2 (up to 17 % in the case of calcium silicate cements [25]. Production of these cement binders at lower temperatures, along with the CO_2 storage capacity, the overall carbon footprint of concrete will be lesser than the OPC concrete, the carbon footprint of carbonated CSC concrete has been reported to be about 70% of OPC concrete [20]. The chemical reactions take place during accelerated carbonation are shown in Equation 4.1 and 4.2 [13].

$$CO_2 + H_20 \leftrightarrows H^+ + HCO_3^- \tag{4.1}$$

$$Ca_x\, Si_y\, O_{(x+2y)} + xH^+ + xHCO_3^- \rightarrow ySiO_2 \downarrow + xCaCO_3 \downarrow + xH_2O \tag{4.2}$$

The effect of carbon dioxide on the accelerated hydration of non-hydraulic and hydraulic di-calcium silicates was studied by few researchers and it was observed that the swift strength development of these compounds was correlated to the rapid development of C-S-H and the possible carbonation reaction is presented in Equation 4.3 [22, 26]

$$2\,(2CaO.SiO_2) + CO_2 + 3H_2O \rightarrow 3CaO.\, 2SiO_2\, .3H_2O + CaCO_3 \tag{4.3}$$

Carbonation of calcium-silicate system is a sequence of reactions; adequate hydration is indispensable to ease the carbonation reaction as most of the reactions befall in the aqueous phase. Carbonic acid forms after the hydration of CO_2 gas, which ionizes by liberating HCO_3^-, CO_3^- and H^+ ions, which drops the pH of solution instantly. This drop in pH accelerates the dissolution of the calcium silicates and releases the SiO_4^{2-} and Ca^{2+} ions in the solution. Under the thermodynamic conditions, these ions recombine and nucleates the C-S-H and calcium carbonate at the same time [27].

Most of the researchers investigated the effect of carbonation on C-S-H developed in results of hydration process of OPC [28, 29], but in the existent literature, the structural properties of carbonation derived C-S-H has not been investigated up to some significant extent [30]. The carbonation of mature concrete is completely different from an early age accelerated carbonation. The early age accelerated carbonation results in the production of C-S-H as shown in Eq. 4.3. On the other hand, the carbonation of hardened concrete during its service life converts the C-S-H to silica gel, which results in the loss of strength and cohesion of concrete [31, 32]. Furthermore, the carbonation of C-S-H is linked to dehydration of C-S-H, more polymerization of silicate chains and decalcification of C-S-H [33, 34].

Calcium carbonate is another major product of accelerated carbonation of calcium-silicate system. The formation of calcium carbonate involves a complex series as a part of the multi-step process following a precipitation-dissolution-precipitation sequence [35]. Aragonite, vaterite, and calcite are the well-known anhydrous polymorphs of calcium carbonate. when conditions are auspicious, the thermodynamically unstable polymorphs (veterite and aragonite) transmutes to calcite which is the most thermodynamically stable polymorph [36, 37].

In this chapter, the microstructural investigation of eco-cement after two hours and twelve hours of carbonation curing to understand the rapid strength development is presented. In addition, SEM/EDS, QXRD, FTIR as well as TGA and TEM were employed to study the nanoscale morphology of reaction products of eco-cement. It is expected that the originality of this work will help to advance specific research in this area, specific to accelerated carbonation of CE and belite in combination, and augmentation in the strength after extended carbonation curing.

4.3. MATERIALS AND METHODOLOGY

4.3.1. MATERIALS

MSW incineration residues used in this research were collected from Emerald Energy from Waste (EFW) in Brampton Ontario. The combustion furnace has two compartments: a lower chamber (temperature between 750-900^oC) and an upper chamber (maximum temperature of 1050^oC). The upper chamber will be investigated for its potential to serve as a furnace for making eco-cement. There is a total of five such furnaces working in series at the facility. Approximately 180,000t of MSW are incinerated annually, leaving behind 30,000t of bottom ash, 500t of vitrified boiler ash and 4,000t of air pollution control (APC) lime residues. Hydrated lime and ground silica sand were used as supplementing additives when needed. Compositional analyses of as-received MSWI residues OPC were carried out using X-ray Fluorescence (XRF) and a Carbon/Sulfur Analyzer, the results of which are presented in Table 4.1. it was observed that the main oxides required for the cement production were available in quite a comparable amount as required to produce OPC. The as-received MSWI residues were dried and sieved first and then proportioned according to the proposed clinker blending proportions and mixed to achieve homogeneity of the blend. As discussed earlier in Chapter 3, M2 mix proportions were decided to be used for further research purposes. Bottom ash, boiler ash, and APC residues were used in a proportion of 28.80%, 28.80%, and 36.04 % respectively. Commercially available $Ca(OH)_2$ and SiO_2 were added by 4.90 % and 1.47% respectively. After proportioning the material, the turn-over rotating ball mill mixer was used to blend the mix. After the exhaustive blending, the blend was pulverized to a fine powder by a ring-and-puck vibratory pulverizer. The pulverized powder was used to produce nodules and were produced using a nodule producer machine by taking a powder to water ration of 0.15. The nodule size was kept in the range of 5mm to 20mm. was operated at 35 rpm, and the process was continued until the spherical nodules were formed. These nodules were then placed in an aluminum boat shaped crucible, and the crucible was positioned in the furnace for clinkering. Clinkering was carried out at a temperature of 1100°C. After the desired clinkering process, the clinkers were left inside the furnace to cool down slowly. After reaching the room temperature, the clinkers were retrieved from the furnace and pulverized again to produce eco-cement. The produced eco-cement was used for all the microscopic characterization presented in this article.

4.3.2. CARBONATION AND COMPRESSIVE STRENGTH TESTING

To study the microstructure of eco-cement (EC) after carbonation activation, paste samples were prepared by mixing 100 g of eco-cement with 9.5 g of water (water to cement ratio was 0.095) in a regular kitchen aid mixer. The cement and water were mixed at a lower speed for 1 minute, the material on the blade and sides were scrapped off and the mixing process was stopped for 30 seconds. Final mixing was carried out in three steps, mixing at medium speed for 1 minute, mixing at high speed for 30 seconds and lastly for 30 seconds at medium speed. The paste was compacted into small cylindrical compacts of 15 mm diameter and 30 mm length by keeping the aspect ratio of 2. For this purpose, MTS- SINTECH 30/G compressive tester equipped with 150 KN load cell machine was used, and maximum consolidation pressure of 5 MPa was applied. Carbonation of the eco-cement compacts was carried out at 152 kPa (22 psi) in an air-tight vessel, using pure CO_2 (99.5%) for the duration ranging from 2 to 24 hours. Carbonation results (weight gain and carbon uptake) were calculated by weighing compacts before and after carbonation. To calculate the CO_2 uptake, the mass of cylindrical compacts was measured before and after the carbonation, using the mass gain during the carbonation and the initial mass of the compacts, the net CO_2 uptake was calculated. For compressive strength measurements, the cylindrical compacts were tested for compressive testing in accordance with ASTM C-39 using MTS- SINTECH machine.

4.3.3. QUANTITATIVE X-RAY DIFFRACTION MEASUREMENTS

To identify the mineral phases and their relative weight percentages Quantitative X-ray diffraction (QXRD) analysis was performed. QXRD patterns of the eco-cement were recorded with Cu Kα radiation on a Siemens D-500 diffractometer. The diffraction pattern was obtained for the range of 2θ angles from 10° to 90° using the step size of 0.02. Cylindrical compacts prepared and cured as discussed in section 4.2 were ground into powder form and the powder was used to perform QXRD analysis.

4.3.4. THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA was conducted to determine the composition of phases and to predict their thermal stability. For the TGA, the carbonated paste samples were crushed and then sieved through number 200 sieve (0.074 mm opening). Commercially available instrument (TA instrument TGA Q500) was used to perform the TGA test. The powder sample was first kept in isothermal condition for 10 min and then the temperature was raised at the rate of 10°C per minute up to 1000°C. Approximately 5 to 10 mg of powder samples were tested. Helium was used as purge gas during TGA tests.

4.3.5. FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR was used to identify the different phases of the samples by the distinctive molecular fingerprint which is produced by infrared absorption spectrum. FTIR spectra were recorded using the Thermo Scientific™ Nicolet™ iS20 FTIR Spectrometer instrument. FTIR spectra were recorded for three curing conditions; eco-cement after clinkering, Eco-cement paste powder after two hours and twelve hours of accelerated carbonation curing. The FTIR absorption spectra were recorded over the range 600 – 4000 cm^{-1} with 2 cm^{-1} resolution.

4.3.6. SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

SEM was used to study the morphology of the samples; the SEM analysis was performed on cylindrical paste specimens. These compacts were randomly broken, a small piece from the broken surface was taken and 4-5 nanometer coating of platinum was applied to avoid the charging effect at high magnifications. Once prepared, the specimens were investigated using a scanning electron microscope (SEM) equipped with the energy dispersive X-ray (EDX) spectrometer operated either in the backscattered electron (BSE) or the secondary electron (SE) modes, depending on the type of examinations performed.

The SEM images and the EDX were obtained by FEI Inspect F50 Field Emission Scanning Electron Microscope (FESEM) operating in high vacuum mode with an accelerating voltage of 15 kV and using the working distance of 10 mm. Along with the SE images collected at different magnification levels, the EDX spectra were also acquired from selected individual points to perform the quantitative X-ray microanalysis. The energy-dispersive spectrometer measures the number and the energy of the X-rays emitted from a specimen. The energies of the X-rays are characteristic of the given chemical element and thus EDS allows for the determination of the elemental composition of the specimen.

4.3.7. TRANSMISSION ELECTRON MICROSCOPY (TEM)

Image morphology of phases at very high magnification was studied by TEM, TEM analysis carbonated eco-cement was conducted on powder specimens obtained by crushing the compacts. High-resolution HR-TEM Tecnai G2F20 STEM, operated at 200 k, equipped with a Gatan Ultrascan 4000 4k CCD camera system, and with Oxford Instrument EDS (energy dispersive spectroscopy) was used to carry out fine microstructural analysis.

4.4. RESULTS AND DISCUSSIONS

4.4.1. EFFECT OF CARBONATION TIME ON COMPRESSIVE STRENGTH AND CO_2 UPTAKE

The effect of carbonation time on compressive strength and CO_2 uptake is presented in Fig. 4.1. The average compressive strength of the compacts after 2-hours of carbonation was measured as 54.3 and average CO_2 uptake was 5.16%. The average compressive strength jumped to 78.8 MPa after 12-hours of carbonation i.e. 48 % higher than the 2-hour strength. On the other hand, the CO_2 uptake after 12-hours of carbonation was increased by only 50 % as compared to the 2-hours carbonation. It was also observed that the strength after 6-hours of carbonation remained the same as compared to the strength after 2-hours carbonation, even though the CO_2 increased by 25%. This showed a plateau-phenomenon, where the CO_2 uptake was increased but the strength was constant, this could be interestingly analogous to the yielding zone of carbon steel stress-strain curve. There could be some phase transformation was taking place in between 2-hours and 12 hours of carbonation curing time. On the other hand, the strength and CO_2 uptake showed almost negligible increment after 18-hours and 24-hours of carbonation curing. The compressive strength was measured to be 77.77 MPa and 79.90 MPa after 18-hours and 24-hours of carbonation respectively. This increase in the strength was quite significant and only observed in the case of eco-cement as there was no such strength increment observed during the carbonation of OPC for prolonged carbonation durations. The cylindrical samples were placed in the water after respective carbonation curing times and were then tested after 28-days and 90-days of hydration, the compressive strength results are presented in Table 4.2. It was observed from the compressive strength results, there was no significant change in the compressive strength of eco-cement. This was indicative of poor hydraulic activity of EC after carbonation. On the other hand, it demonstrated eco-cement was not water soluble against water exposure. The eco-cement activated by 2-hours and 12-hours carbonation will be analyzed in detail in the following sections.

4.4.2. QUANTITATIVE X-RAY DIFFRACTION (QXRD) ANALYSIS RESULTS

QXRD analysis results of eco-cement powder before and after carbonation is presented in Table 4.3. The major phase identified in the eco-cement was chlorellestadite (CE) ($Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$). It was also observed that the two major CO_2-reactive phases identified were CE and Larnite (Ca_2SiO_4), the other minor CO_2-reactive phase was Wadalite ($Ca_6Al_5Si_2O_{16}Cl_3$). CE was the phases which had trapped chlorine, but both CE and larnite phases were CO_2-reactive. Reduction in CE was 52.5 % after 2-hours of carbonation, and 77% after 12 h carbonation. On the other hand, larnite reacted with CO_2 and its reduction reached 33 % and 68% after carbonation of 2-hours and 12- hours respectively. Other phases such as quartz, halite, and sylvite were found to be non-CO_2-reactive or very low CO_2-reactive, with almost negligible reduction as comparing the mass before and after carbonation. Reaction products of carbonation of eco-cement also included gypsum, vaterite, and the X-ray insensitive phase (amorphous phase) which counted for a significant increase. Therefore, these results strongly suggest that the binding matrix which is responsible for the high strength probably was a combination of $CaCO_3$, gypsum and Ca-Si intermix (C-S-H-like).

4.4.3. THERMOGRAVIMETRIC TEST RESULTS

Fig. 4.2 shows thermogravimetric (TG) curves for the as-produced eco-cement, the 2h carbonated eco-cement paste, and the 12h carbonated eco-cement paste. The as-produced eco-cement had not shown any mass loss up to almost 750°C, which was quite logical as there was no entrapped or free water and other hydrated pastes such as CaOH or $CaCO_3$. But there was a rapid drop after 800°C which is about 9 % of the mass, this drop was also observed in carbonated samples. This reason for the rapid drop could be the decomposition of the CE phase. Fig. 4.3 shows DTG curves together with TG. In case of carbonated eco-cement pastes (Fig. 4.3(b) and 4.3(c)), there was a continuous mass loss over the entire range of test temperature (i.e., from 23°C to 1000°C). The mass losses were calculated and tabulated in Table 4.3. The largest mass loss was observed in the temperature range from about 500°C to 700°C. The mass loss in the temperature region of 500°C to 700°C is attributed to the decomposition of $CaCO_3$. The mass loss at the temperature of 100°C indicated the loss of both, physically and chemically bound water present in the gel phases. The mass loss at 110°C confirmed the presence of gypsum.

4.4.4. FOURIER-TRANSFORMATION INFRARED SPECTROSCOPY RESULTS

FTIR spectra for the raw and carbonated eco-cement powder is presented in Fig. 4.4. The major vibrational bands identified from the eco-cement (Fig. 4.4) were: $_{V3}$ SiO_4^{4-}, (asymmetric Si-O stretching), centered at around 935 cm^{-1}. The triplet bands appearing at 1100-1130 cm $^{-1}$ were due to the $_{v3}$ modes of SO_4^{2-} and the weak band at 658 cm-1 was due to $_{v4}$ modes of SO_4^{2-}. The band assignments were in good agreement with those reported by others [38, 39]. The SO_4^{2-} peaks 671 cm-1 and Ca-O peak at pointed towards the presence of CE in all the samples. When eco-cement paste was exposed to accelerated carbonation for two and twelve hours, a very intense peak appeared at 1420-1430 cm^{-1} due to $_{v3}$ CO_3^{2-} and a sharp band appeared at 870 cm^{-1} corresponding to $_{v2}$ CO_3^{2-}. The $_{V3}$ SiO_4^{4-} peak appearing at 935 cm^{-1} in the eco-cement was shifted to the higher energy field centered between 1030-1076 cm^{-1}. The shifting of $_{V3}$ $SiO_4^{4-}$to the higher energy field was indicative of polymerization of the orthosilicate units, SiO_4^{4-}, present in Eco-cement matrix and was attributed to the formation of C-S-H [40]. The prominence of the OH-band in accelerated carbonation samples provided evidence for the reaction of gypsum. Thus, the FTIR spectra confirmed the presence of C-S-H, $CaCO_{3,}$ and gypsum in the carbonated samples.

4.4.5. SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

SEM micrographs taken at 10,000 magnifications of unreacted eco-cement is presented in Fig. 4.5. The hexagonal rod-like crystals of unreacted CE was observed and those were confirmed by EDS and presented in spot “A”. EC has needle-like hexagonal crystals as described by S. J. Saint-Jean et. al. during their research on the presence of CE in the preheat system of cement kilns [19]. Spot

"B" of Fig. 4.5 represents a complex phase having sodium, aluminum, chlorine, and calcium. This showed that the salts were bonded with calcium aluminate phases during the clinkering process. The micrographs and EDS of carbonated eco-cement pastes are presented in Fig. 4.6-4.8. From the physical microstructure presented in Fig. 4.6 and Fig. 4.7, it was observed that the structure after 2-hours carbonation had more unreacted hexagonal crystals of EC. In addition to that, the physical porosity and absence of cohesion and compactness were also observed in the micrographs of the 2-hours carbonated sample (Fig. 4.6). On the other hand, from Fig. 4.7, which represents the micrograph of the sample after 12-hours carbonation. Almost all of the CE crystals were reacted, and compactness of the microstructure was observed. The reaction of CE crystals was observed to be directly proportional to the carbonation time i.e. the more the carbonation exposure, the higher the reaction and lesser the amount of CE in the samples. This phenomenon was confirmed by the QXRD results as presented in Table 4.2. From the appearance of micrographs, it can be observed that the physical porosity is reduced to a great extent after twelve hours of carbonation as compared to the two hours of carbonation curing, as the growth of microstructure had covered all the spaces. Mechanical interlocking and friction seemed to be increased in twelve hours carbonated samples as compared to the two hours carbonation samples, that could be another reason in the strength increment after 12-hours carbonation. EDS analysis of 2-hours and 12-hours carbonated sample are presented in Fig. 4.6 and 4.7 respectively. After 2-hours carbonation, most of the CE crystals were present having a large amount of Chlorine and Sulfur which can be observed in spot "A" of Fig. 4.6, but with the carbonation the hexagonal CE crystals were converted to another shape of microstructure with negligible to no amount of chlorine and sulfur as shown in spot "B" of Fig. 4.6. These microstructure spots are most likely to be calcium silicate hydrocarbonate phase with some amount of carbon present, if all the chlorine and sulfur is released from CE, the new phase most likely to be carbon calcium silicate hydrocarbonate, because eco-cement is a non-hydraulic cement binder, so the presence of pure C-S-H phase is almost impossible. On the other hand, the 12-hours carbonated sample showed more reactivity of CE crystals, the chlorine and sulfur were not detected in fully reacted crystals of CE (Fig. 4.7 spot "A"), and the carbonated calcium silicates oxides were observed in higher amounts. The hydrated phases found in OPC could not be compared with the phases available in the carbonated eco-cement. There could be two reasons of this phenomenon; firstly, the raw meal of eco-cement was not as pure as the raw meal of OPC; secondly, eco-cement had a carbonation activation and non-hydraulic behavior as compared to the OPC. Presence of gypsum was also observed in carbonation cured eco-cement as presented in spot "B" of Fig. 4.7.

To study the CE crystal structure, change due to carbonation, the eco-cement powder was carbonated for twelve hours to simulate eco-cement compact carbonation and examined under a scanning electron microscope at higher magnification. Carbonation time of twelve hours was chosen based on the strength development mechanism because eco-cement paste showed the highest compressive strength after twelve hours of carbonation. It was interesting to know the corresponding crystalline structure. Fig. 4.8 represents the micrographs with EDS of twelve hours carbonated eco--Cement powder at higher magnifications, lower magnification morphology is presented in Fig. 4.8(a), and Fig. 4.8(b) shows the morphology and EDS at higher magnifications. It was observed from Fig. 4.8 (a) and 4.8(b), that the microstructure of CE crystal changes completely after reacting with the CO_2 and converted to another spindle and fibrillar amorphous phase from original hexagonal shape. This spindle and fibrillar shaped microstructures grow and density with an extended carbonation duration. The dimensions of these shapes are in the range of nanometer to micrometers, the morphology of these shapes at higher magnification was analogous to nano-particles packed in a similar way as observed by the packing model of C-S-H proposed by Jennings [41]. Furthermore, the EDS analysis of these fibrillar structures showed that these were mainly composed of low Ca, high Si, high C and abundant O, leading to a new amorphous phase of low lime calcium-silicate-hydrocarbonate modified by S, Cl, and alkali.

4.4.6. TEM RESULTS

TEM analysis was only carried out for the twelve hours carbonation cured eco-cement paste, which showed the maximum compressive strength development, and was the indicator of maximum carbonation reaction of eco-cement. The amorphous phase and a crystalline phase can be observed from Fig. 4.9(a), the EDS of crestline phase (spot "A") indicated the presence of $CaCO_3$ and the EDS of amorphous phase (spot "B") confirmed the formation of calcium silicate hydrocarbonate. Spot "C" showed the presences of $CaCO_3$ as well, and there are some other crystals are present under the crystals of CaCO3, that is why the morphology of spot "A" is different than spot "B". Moreover, the Selected Area (electron) Diffraction (SAED) of spot did not show any lattice of the crystal, which could be considered as an amorphous site. From the TEM analysis, this observation can be made that the major reaction products were calcium silicate carbo-hydrates and $CaCO_3$, the major contributor to the strength development of eco-cement.

4.5. SUMMARY AND OBSERVATIONS

In this research, eco-cement was produced from MSWI residues and it was carbonated for different durations. The microstructure was studied using different techniques and the conclusions of the research are summarized below:

i. Carbonation curing duration enhanced the compressive strength, and it demonstrated a positive effect on the compressive strength of eco-cement. The 12-hours carbonation strength was 50% higher than the 2-hours carbonation strength of eco-cement.

ii. Carbonation activation by twelve hours had significantly improved the microstructure as compared with two hours carbonation activation. CE crystals were decreased and can be observed physically, and the amorphous nano-sized fibrillary structures were increased. The denser microstructure was observed, and the maximum amount of CE was converted into a new phase.

iii. QXRD identified the CE and belite as the major carbonation reactive phases, carbonation curing of these phases resulted in the formation of $CaCo_3$, gypsum, an increase in the amorphous phase. The amorphous phase was most likely to be a calcium silicate hydrocarbonate.

iv. TGA and FTIR confirmed the presence of calcium carbonate, gypsum, and calcium silicate hydrocarbonate.

v. SEM/EDS showed the packing density and reactivity of twelve hours carbonation curing is much better than two hours carbonation curing. The presence of amorphous calcium silicate hydrocarbonate phase was also observed by SEM/EDS.

vi. TEM analysis helped to confirm the presence amorphous phase (calcium silicate hydrocarbonate) and $CaCO_3$ were also identified in TEM micrographs, which reveals that carbonation derived a matrix of eco-cement is mainly composed of amorphous calcium silicate hydrocarbonate.

vii. It was observed that the superior binding strength of carbonated eco-cement is due to the combination of mechanical and chemical actions. Chemical action includes the formation of calcium carbonate, calcium silicate hydrocarbonate, and gypsum. Mechanical action consists of high packing density along with the friction bond of nanoparticles of fibrillar shaped microstructure produced by carbonation of CE, leading to a dense microstructure after prolonged carbonation curing.

REFERENCES

1. Hoornweg, D. and P. Bhada-Tata, *What a waste: a global review of solid waste management.* What A Waste: A Global Review of Solid Waste Management, 2012.
2. Stehlík, P., *Contribution to advances in waste-to-energy technologies.* Journal of Cleaner Production, 2009. **17**(10): p. 919-931.
3. Tang, J., R. Ylmén, M. Petranikova, C. Ekberg, and B.M. Steenari, *Comparative study of the application of traditional and novel extractants for the separation of metals from MSWI fly ash leachates.* Journal of Cleaner Production, 2018. **172**: p. 143-154.
4. Erol, M., S. Küçükbayrak, and A. Ersoy-Meriçboyu, *Production of glass-ceramics obtained from industrial wastes by means of controlled nucleation and crystallization.* Chemical Engineering Journal, 2007. **132**(1-3): p. 335-343.
5. Lederer, J., V. Trinkel, and J. Fellner, *Wide-scale utilization of MSWI fly ashes in cement production and its impact on average heavy metal contents in cements: The case of Austria.* Waste Management, 2017. **60**: p. 247-258.
6. Cheng, T.W., M.Z. Huang, C.C. Tzeng, K.B. Cheng, and T.H. Ueng, *Production of coloured glass-ceramics from incinerator ash using thermal plasma technology.* Chemosphere, 2007. **68**(10): p. 1937-1945.
7. Guo, X., H. Shi, W. Hu, and K. Wu, *Durability and microstructure of CSA cement-based materials from MSWI fly ash.* Cement and Concrete Composites, 2014. **46**: p. 26-31.
8. Shi, H.s., K. Deng, F. Yuan, and K. Wu, *Preparation of the saving-energy sulphoaluminate cement using MSWI fly ash.* Journal of Hazardous Materials, 2009. **169**(1-3): p. 551-555.
9. Saikia, N., S. Kato, and T. Kojima, *Production of cement clinkers from municipal solid waste incineration (MSWI) fly ash.* Waste Management, 2007. **27**(9): p. 1178-1189.
10. Ghouleh, Z. and Y. Shao, *Turning municipal solid waste incineration into a cleaner cement production.* Journal of Cleaner Production, 2018. **195**: p. 268-279.
11. Fang, Y.N., C. Ritter, and T.J. White, *Crystal chemical characteristics of ellestadite-type apatite: Implications for toxic metal immobilization.* Dalton Transactions, 2014. **43**(42): p. 16031-16043.

12. Saint-Jean, S.J., E. Jøns, N. Lundgaard, and S. Hansen, *Chlorellestadite in the preheater system of cement kilns as an indicator of HCl formation.* Cement and Concrete Research, 2005. **35**(3): p. 431-437.

13. Ashraf, W., J. Olek, and J. Jain, *Microscopic features of non-hydraulic calcium silicate cement paste and mortar*. Cement and Concrete Research, 2017. **100**: p. 361-372.

14. Development, W.B.C.f.S., *Cement Technology Roadmap 2009: Carbon Emissions Reductions Up to 2050*. 2009.

15. Shen, L., T. Gao, J. Zhao, L. Wang, L. Wang, L. Liu, F. Chen, and J. Xue, *Factory-level measurements on CO2 emission factors of cement production in China.* Renewable and Sustainable Energy Reviews, 2014. **34**: p. 337-349.

16. Geological Survey, U.S., *Miner. Commod. Summ.* Miner. Commod. Summ., 2017.

17. Scalenghe, R., F. Malucelli, F. Ungaro, L. Perazzone, N. Filippi, and A.C. Edwards, *Influence of 150 years of land use on anthropogenic and natural carbon stocks in emilia-romagna region (Italy).* Environmental Science and Technology, 2011. **45**(12): p. 5112-5117.

18. Gartner, E. and T. Sui, *Alternative cement clinkers*. Cement and Concrete Research, 2017.

19. Riman, R.E., T.E. Nye, V. Atakan, C. Vakifahmetoglu, Q. Li, and L. Tang, *Synthetic formulations and methods of manufacturing and using thereof.* Synthetic Formulations and Methods of Manufacturing and Using Thereof, 2015.

20. Sahu, S. and N. DeCristofaro, *Solidia Cement™, Solidia Technologies. White Paper.* 2013.

21. Ashraf, W. and J. Olek, *Carbonation behavior of hydraulic and non-hydraulic calcium silicates: potential of utilizing low-lime calcium silicates in cement-based materials.* Journal of Materials Science, 2016. **51**(13): p. 6173-6191.

22. Bukowski, J.M. and R.L. Berger, *Reactivity and strength development of CO2 activated non-hydraulic calcium silicates.* Cement and Concrete Research, 1979. **9**(1): p. 57-68.

23. Jang, J.G. and H.K. Lee, *Microstructural densification and CO2 uptake promoted by the carbonation curing of belite-rich Portland cement.* Cement and Concrete Research, 2016. **82**: p. 50-57.

24. Qian, B., X. Li, and X. Shen, *Preparation and accelerated carbonation of low temperature sintered clinker with low Ca/Si ratio.* Journal of Cleaner Production, 2016. **120**: p. 249-259.

25. Ashraf, W., J. Olek, and V. Atakan. *Carbonation reaction kinetics, CO2 sequestration capacity, and microstructure of hydraulic and non-hydraulic cementitious binders*. in *Sustainable Construction Materials and Technologies*. 2016.

26. Young, J.F., R.L. Berger, and J. Breese, *Accelerated Curing of Compacted Calcium Silicate Mortars on Exposure to CO<inf>2</inf>.* Journal of the American Ceramic Society, 1974. **57**(9): p. 394-397.

27. Fernández Bertos, M., S.J.R. Simons, C.D. Hills, and P.J. Carey, *A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2.* Journal of Hazardous Materials, 2004. **112**(3): p. 193-205.

28. Garg, N., *Raman spectroscopy for characterizing and determining the pozzolanic reactivity of fly ashes.* Raman Spectroscopy for Characterizing and Determining the Pozzolanic Reactivity of Fly Ashes, 2012.

29. Ha, J., S. Chae, K.W. Chou, T. Tyliszczak, and P.J.M. Monteiro, *Scanning transmission X-ray microscopic study of carbonated calcium silicate hydrate*, in *Transportation Research Record*. 2010. p. 83-88.

30. Ghouleh, Z., R.I.L. Guthrie, and Y. Shao, *High-strength KOBM steel slag binder activated by carbonation.* Construction and Building Materials, 2015. **99**: p. 175-183.

31. Pellenq, R.J.M., N. Lequeux, and H. van Damme, *Engineering the bonding scheme in C-S-H: The iono-covalent framework.* Cement and Concrete Research, 2008. **38**(2): p. 159-174.

32. Black, L., C. Breen, J. Yarwood, K. Garbev, P. Stemmermann, and B. Gasharova, *Structural features of C-S-H(I) and its carbonation in air-A Raman spectroscopic study. Part II: Carbonated phases.* Journal of the American Ceramic Society, 2007. **90**(3): p. 908-917.

33. Jennings, H.M., *A model for the microstructure of calcium silicate hydrate in cement paste.* Cement and Concrete Research, 2000. **30**(1): p. 101-116.

34. Black, L., K. Garbev, and I. Gee, *Surface carbonation of synthetic C-S-H samples: A comparison between fresh and aged C-S-H using X-ray photoelectron spectroscopy.* Cement and Concrete Research, 2008. **38**(6): p. 745-750.

35. Gal, J.Y., Y. Fovet, and N. Gache, *Mechanisms of scale formation and carbon dioxide partial pressure influence. Part II. Application in the study of mineral waters of reference.* Water Research, 2002. **36**(3): p. 764-773.

36. Wehrmeister, U., D.E. Jacob, A.L. Soldati, N. Loges, T. Häger, and W. Hofmeister, *Amorphous, nanocrystalline and crystalline calcium carbonates in biological materials.* Journal of Raman Spectroscopy, 2011. **42**(5): p. 926-935.

37. Goto, S., K. Suenaga, T. Kado, and M. Fukuhara, *Calcium Silicate Carbonation Products.* Journal of the American Ceramic Society, 1995. **78**(11): p. 2867-2872.

38. Gard, J.A. and H.F.W. Taylor, *Calcium silicate hydrate (II) ("C-S-H(II)").* Cement and Concrete Research, 1976. **6**(5): p. 667-677.

39. Ghosh, S.N. and S.K. Handoo, *Infrared and Raman spectral studies in cement and concrete (review).* Cement and Concrete Research, 1980. **10**(6): p. 771-782.

40. Mollah, M.Y.A., Y.N. Tsai, T.R. Hess, and D.L. Cocke, *An FTIR, SEM and EDS investigation of solidification/ stabilization of chromium using portland cement Type V and Type IP.* Journal of Hazardous Materials, 1992. **30**(3): p. 273-283.

41. Jennings, H.M., *Refinements to colloid model of C-S-H in cement: CM-II.* Cement and Concrete Research, 2008. **38**(3): p. 275-289.

Table 4.1: Chemical compositions of MSWI residues and OPC

Compounds	**APC Lime** **%**	**Boiler Ash** **%**	**Bottom Ash** **%**	**OPC** **%**
CaO	55.47	18.31	12.71	63.53
Fe_2O_3	0.15	2.19	4.81	2.79
SiO_2	1.79	10.05	25.91	21.64
Al_2O_3	0.17	4.1	10.57	4.42
Na_2O	0.41	8.83	2.09	DL
K_2O	0.49	6.52	1.16	0.55
P_2O_5	0.13	1.4	1.44	0.25
Cl	17.3	6.21	1.59	--
TiO_2	0.09	1.69	2.17	0.27
MnO	0.01	0.07	0.44	0.06
MgO	1.06	1.57	1.81	2.79
S-total	0.43	10.9	0.6	1.60
C-total	1.97	0.02	23.7	0.32
LOI	18.37	0.02	23.7	0.52

Table 4.2 Compressive strength results of eco-cement after different carbonation curing time and subsequent hydration

Sr. #	Carbonation curing time	Carbon uptake (%)	Avg. strength (Mpa) Control	 2 hours	 28 Days	 90 Days
1	2	5.16	1.10	53.35	55.02	55.40
2	6	6.50	1.12	50.57	51.20	52.00
3	12	7.75	1.30	78.80	80.30	81.30
4	18	7.80	1.70	77.77	79.20	79.00
5	24	8.00	1.79	79.90	80.20	80.35

2 hours: after 2h carbonation curing 28 Days and 90 Days: Subsequent hydration of 28 days and 90 days after 2h carbonation

Table 4.3: Quantitative phase analysis of eco-cement before and after carbonation activation via QXRD

Compound	**Formula**	**Eco-cement (%)**	**Eco-cement After 2h CO_2 activation (%)**	**Eco-cement after 12h CO_2 activation (%)**
Chloro-Ellestadite	$Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$	43.8	20.8	10.25
Wadalite	$Ca_6Al_5Si_2O_{16}Cl_3$	6.4	6.2	5.85
Bredigite	$Ca_7Mg(SiO_4)_4$	5.0	4.8	4.75
Quartz	SiO2	0.5	0.4	0.4
Halite	NaCl	2.9	2.0	1.95
Sylvite	KCl	1.4	0.9	1.0
Belite	Ca_2SiO_4	9.6	6.5	3.10
Gypsum	CaSO4.2(H2O)	n.d.	7.4	8.40
Vaterite	CaCO3	n.d.	4.2	6.20
X-Ray insensitive	Amorphous	30.4	46.8	58.1

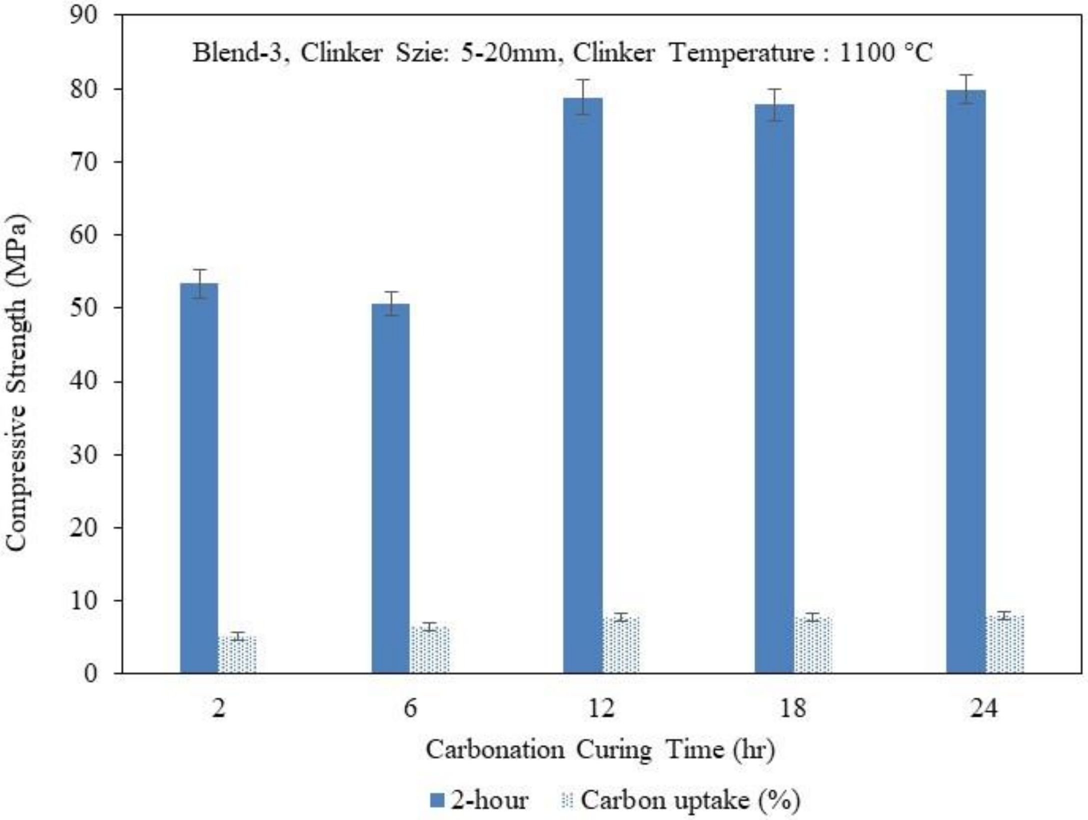


FIGURE 4.1: COMPRESSIVE STRENGTH AND CARBON UPTAKE RESULTS OF ECO-CEMENT AFTER DIFFERENT CARBONATION CURING TIMES (28-DAY HYDRATION STRENGTH OF OPC =54 MPA)

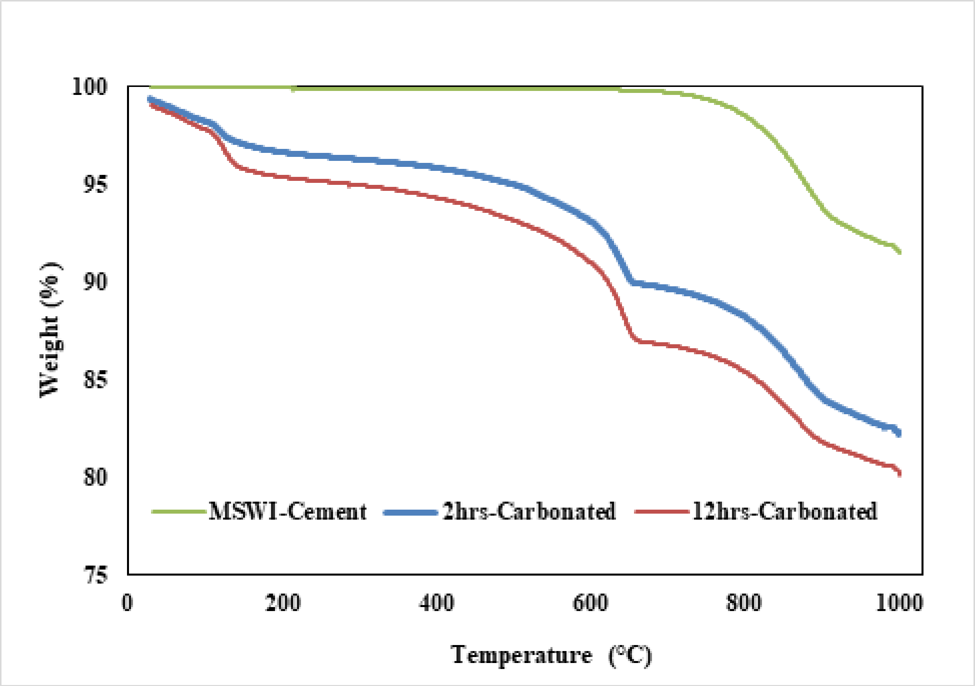
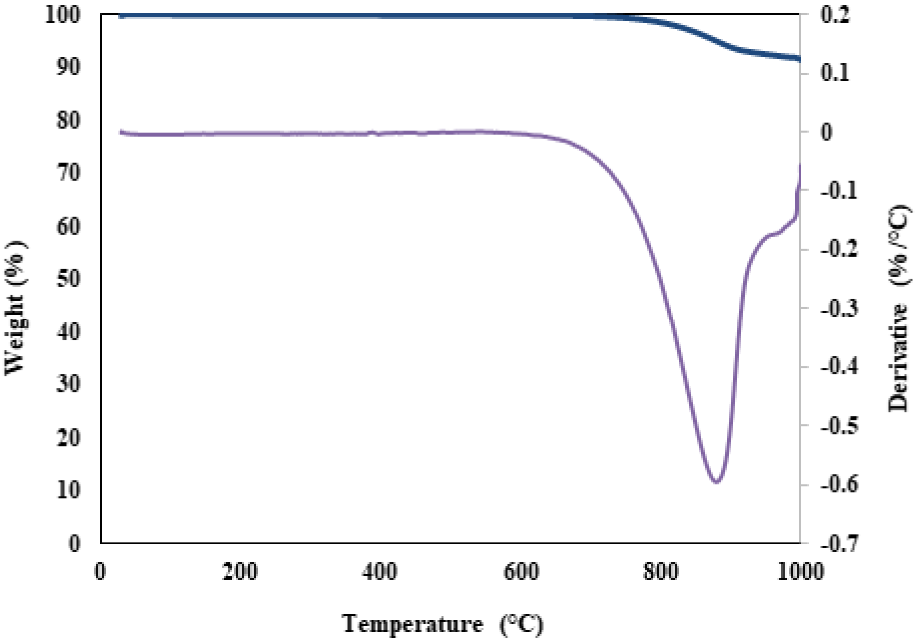
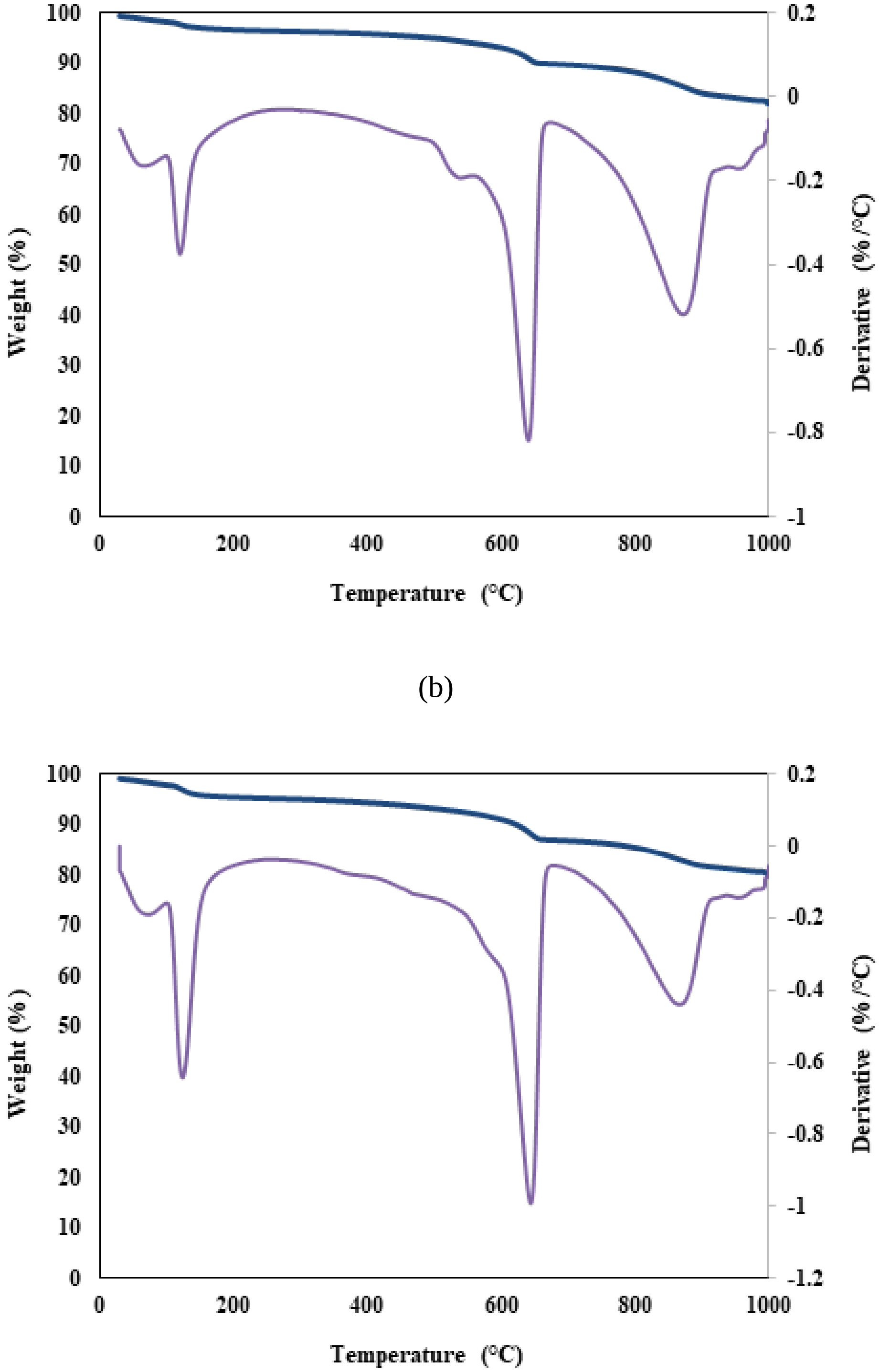


FIGURE 4.2: TGA CURVES FOR ECO-CEMENT BEFORE AND AFTER CARBONATION



(a)



(b)

(c)

FIGURE 4.3: TGA AND DTG ANALYSIS OF (A): ECO-CEMENT (B): AFTER 2H CARBONATION CURING (C): AFTER 12H CARBONATION CURING

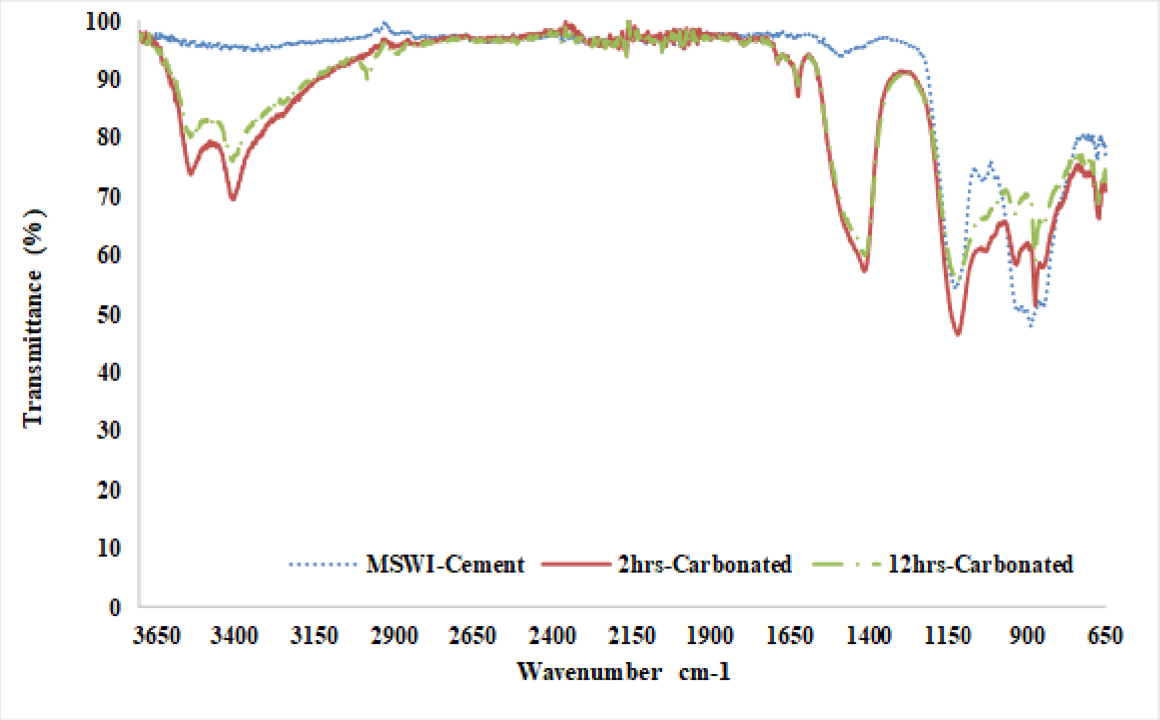


FIGURE 4.4: FTIR SPECTRA OF RAW AND CARBONATED ECO-CEMENT PASTE

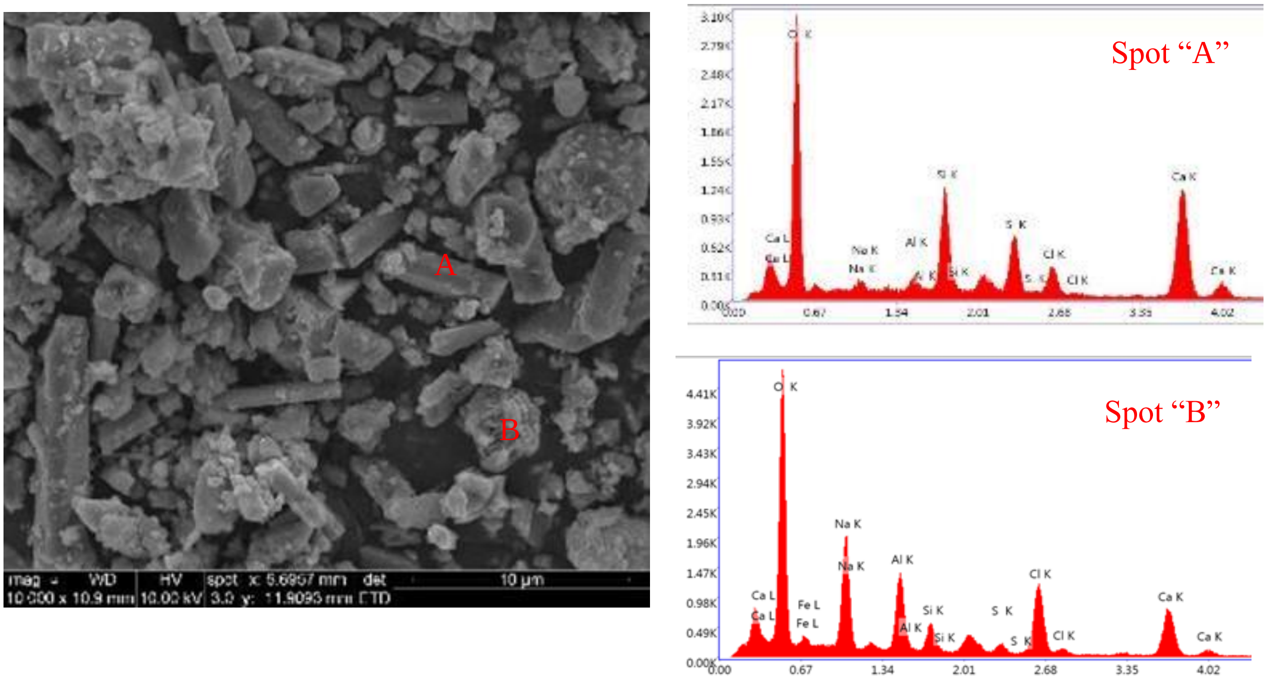


FIGURE 4.5: SEM/EDS OF ECO-CEMENT

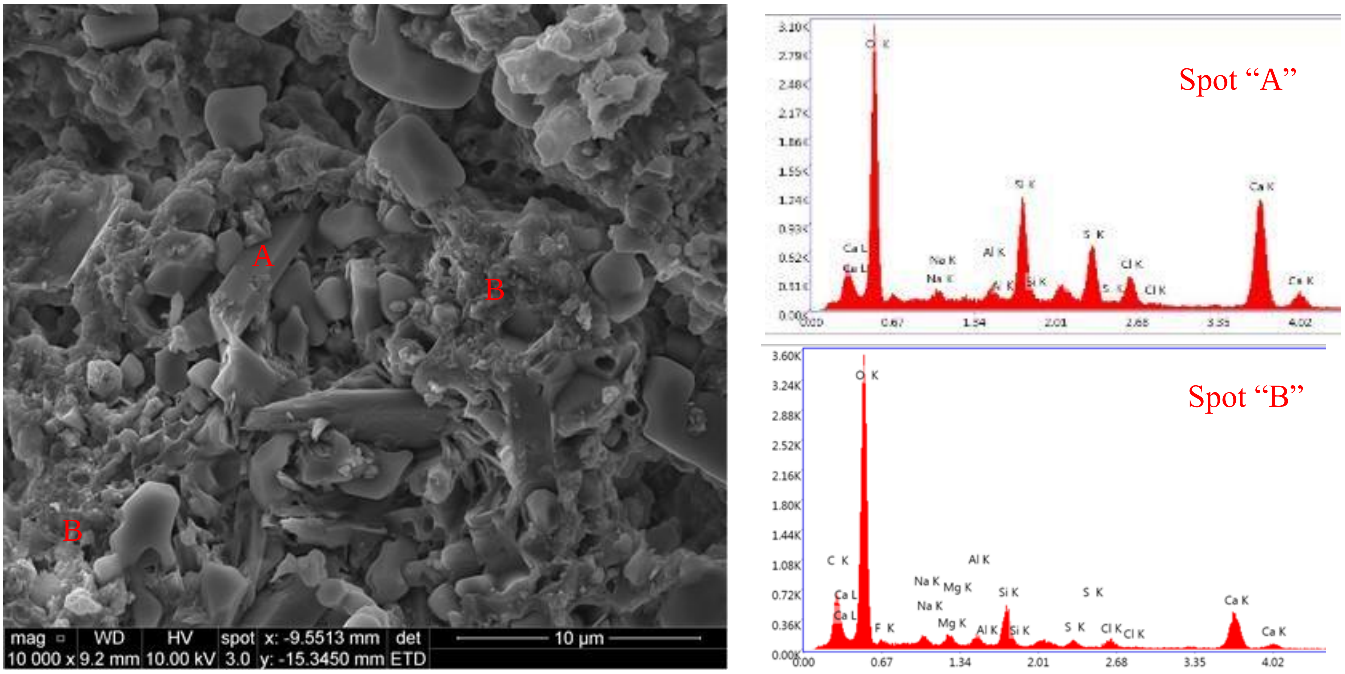


FIGURE 4.6: SEM/EDS OF 2HRS-CARBONATED ECO-CEMENT PASTE

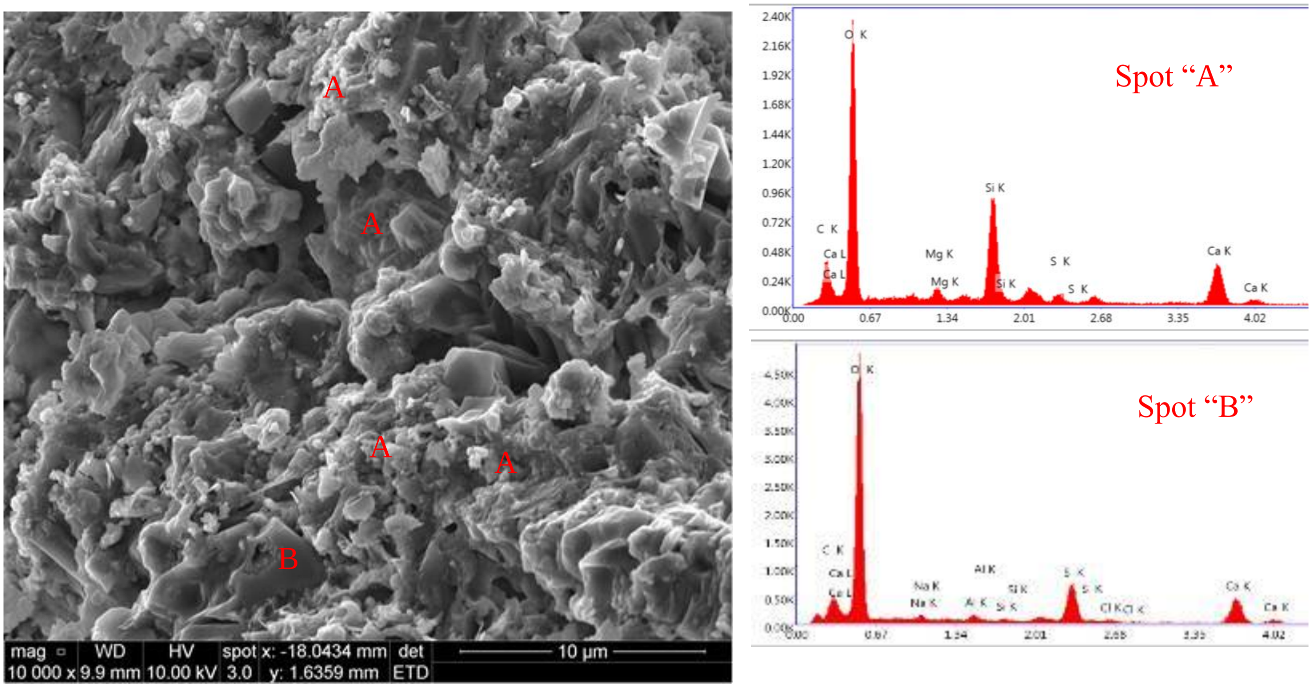
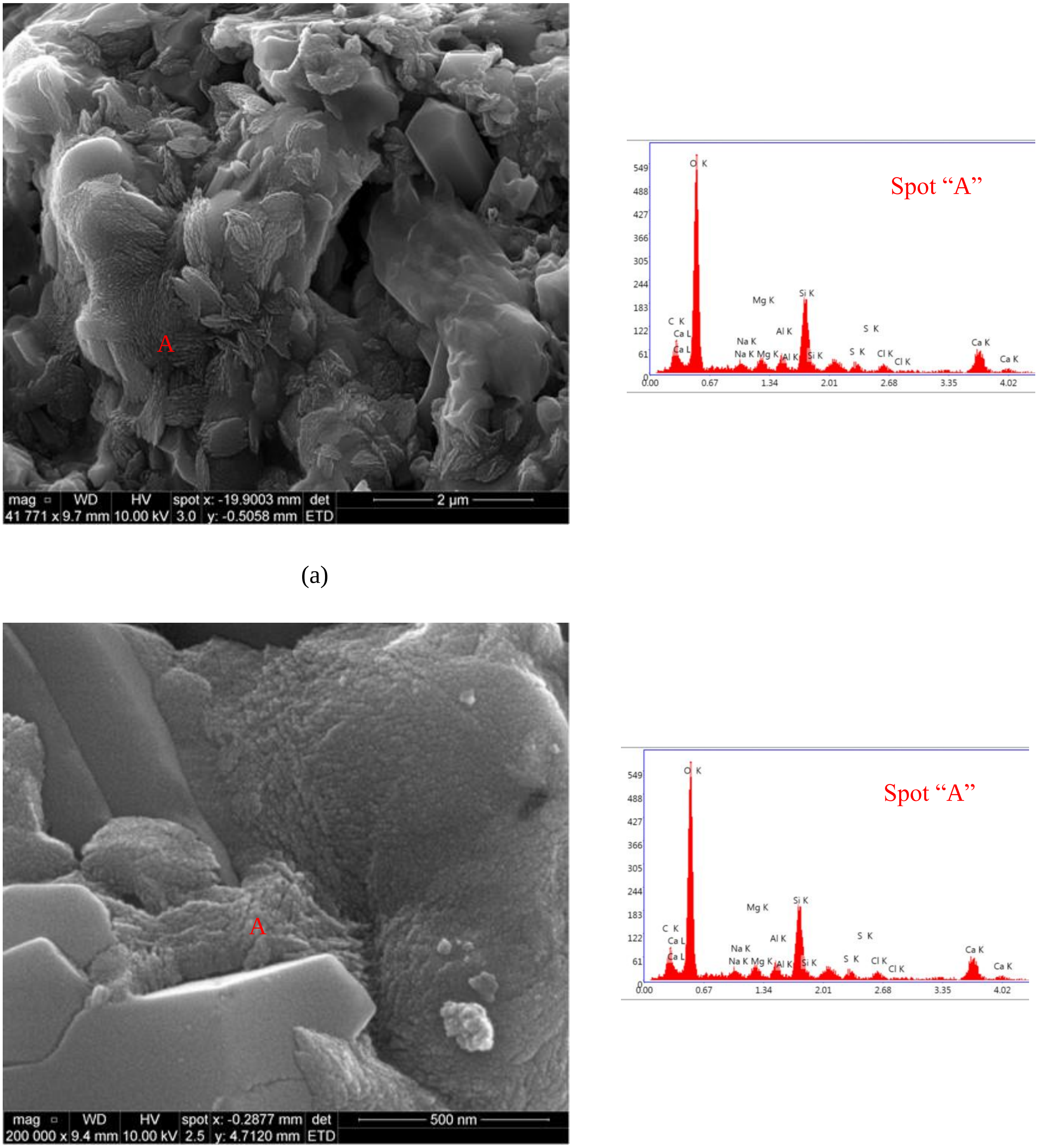


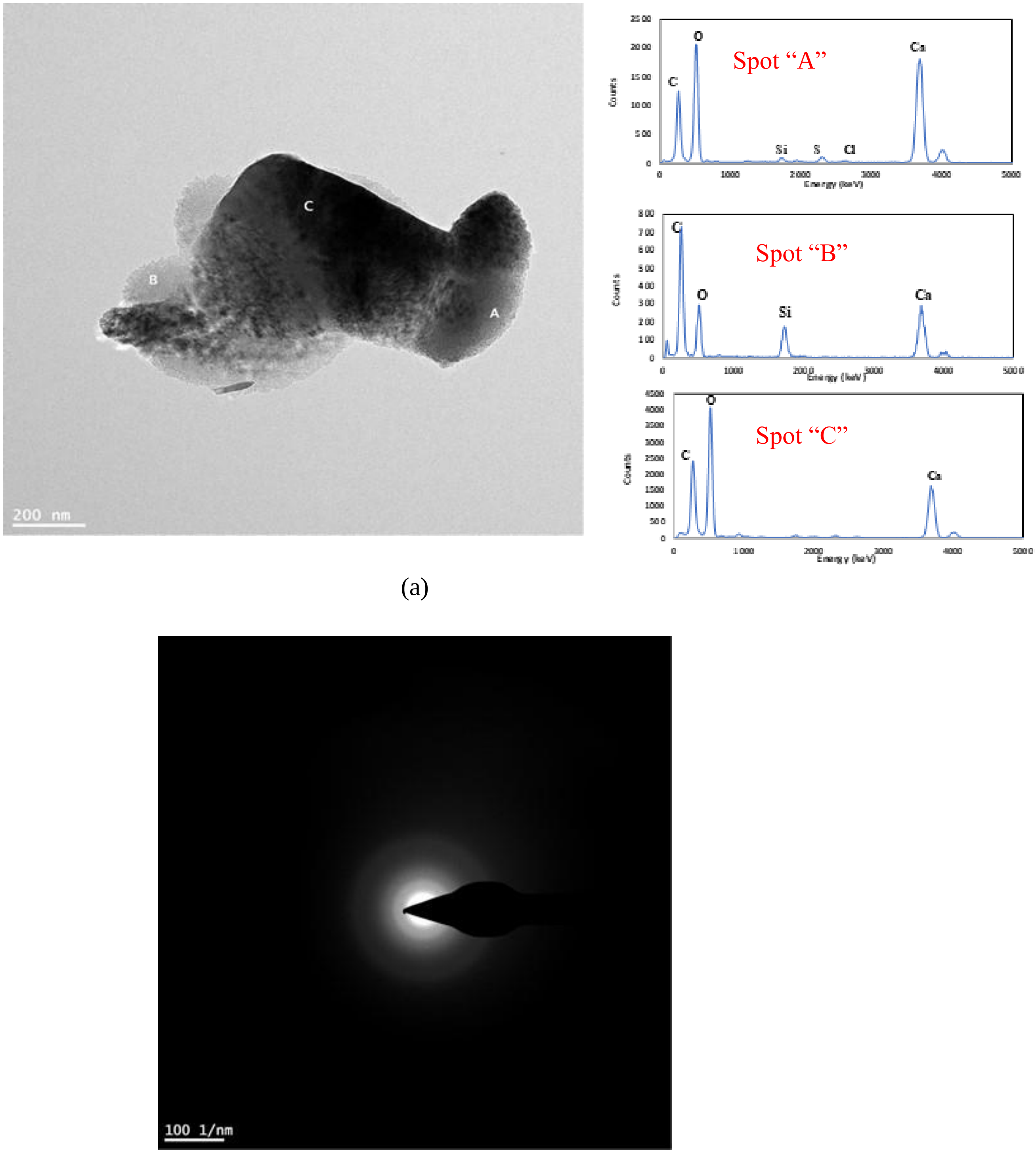
FIGURE 4.7: SEM/EDS OF 12HRS-CARBONATED ECO-CEMENT PASTE



(a)

(b)

Figure 4.8: SEM/EDS of co-cement paste after 12hrs-carbonation (a): Low magnification (b): High magnification



(a)

(b)

4.9: TEM images of 12hrs-carbonated Eco-cement paste (a): TEM/EDS (b): SAED of spot “B”

CHAPTER 5. SYNTHESIS AND CHARACTERIZATION OF CHLORELLESTADITE AND BELITE TO SIMULATE ECO-CEMENT MADE FROM MUNICIPAL SOLID WASTE INCINERATION RESIDUES

PREFACE

Production of eco-cement from the municipal solid waste incineration (MSWI) residue was discussed comprehensively in Chapter 3, and the characterization of the reaction products was presented in Chapter 4. As discussed in Chapter 4, Chlorellestadite (CE) and belite were the two carbonation reactive compounds and the major contributors to the strength development as well. Some other compounds were also detected, most of them were either remained unreactive during accelerated carbonation or reacted negligibly. The reaction products of CE and belite were the major contributors to the strength development of the eco-cement. Interestingly, there is no research available about the carbonation reactivity of CE, and limited literature available to understand the carbonation-derived calcium silicate hydrate as a reaction product of belite. To understand the carbonation reaction of eco-cement and its strength development mechanism, this chapter will synthesize the CE and belite compounds will perform carbonation activation of CE, belite and their combination. The microstructure of carbonated CE, belite and their combination will be characterized by TG, QXRD, and SEM which will ultimately lead towards the better understanding of rapid strength mechanism of eco-cement. Furthermore, it will also help to rationalize the hypothesis presented in Chapter 4, which suggests the formation of amorphous calcium silicate hydrocarbonate, as a modified C-S-H by carbonate and the mechanism of strength development of eco-cement. To accomplish these objectives, the Synthesized pure CE and belite powders were produced, these powders were used to prepare the sample for compressive strength and microstructural studies. The major and the novel contribution of this chapter is to provide evidence about the reaction products formed during the accelerated carbonation of CE. The second contribution is to comprehensively understand the strength mechanism MSWI residues derived eco-cement.

5.1. ABSTRACT

Carbonation activated non-hydraulic eco-cement was derived from the municipal solid waste incineration residues. Microstructural studies of eco-cement showed that the chlorellestadite (CE) and belite were the major carbonation reactive and strength contributing compounds. To understand the strength development mechanism and the reaction products, pure CE and belite were synthesized. The synthesized CE and belite were then mixed to a proportion to simulate the eco-cement. The mixture of CE and belite as well as each component were carbonated two hours and twelve hours to understand the contribution of each component to the ultimate strength gain. CE and belite showed the lower strengths individually but demonstrated a substantial increase in compressive strength when mixed together in a similar manner they were present in eco-cement. Quantitative X-Ray Diffraction (QXRD) analysis confirms the formation of calcium carbonate, gypsum and an increase in amorphous phase (carbon modified C-S-H). SEM/EDS studies also showed the existence of multifaceted calcium silicate phase which was likely the amorphous calcium silicate hydrocarbonate. It was observed that the strength development is a result of multiple chemical and mechanical actions, calcium carbonate and modified calcium silicates contributed chemically and packing of spandrel shaped reaction product of CE contributed mechanically by providing high density at micro-nano scale.

Keywords: Eco-cement, synthesized chlorellestadite, synthesized belite, accelerated carbonation

5.2. INTRODUCTION

Millions of tons of municipal solid waste (MSW) is produced every year, either incinerated or landfilled [1, 2]. Incineration reduces the volume of the waste and produces energy, but incinerated residues require special landfill sites because of hazardous contaminations [3, 4]. On the other hand, these municipal solid waste incineration (MSWI) residues are very rich in lime and silica and have great potential to be used as a raw meal for cement production [3, 5]. Efforts were made to produce cement binder by using these MSWI residues up to 20-60 % of the raw feed and the clinkering temperature was varied between 1100°C to 1400°C. [5-10]. Non-hydraulic carbon reactive cement binder is developed recently by using MSWI residues 85 % to 100 % of the raw feed [11]. Chlorellestadite ($Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$) was found to be the major compound produced during the clinkering process, and it was found to be the most CO_2 reactive phase. Belite was also identified as the second major CO_2 reactive phase [11]. Ellestadite could be found with different end chain members, and it is a member of the apatite group. Usually, ellestadites are named after the end chain members, such as if end chain member is Cl it is termed as chlorellestadite. The same is true for the F (Fluor-ellestadite), and OH (hydroxyl-ellestadite) [12, 13]. The presence of Si, Ca, Cl and S in the MSWI residues and clinkering temperature of 1100°C facilitated the production of CE [11, 14]. CE is a non-hydraulic compound and exhibited water insolubility, but remarkably it showed very high carbonation reactivity [11, 14]. The results presented in Chapter3 and 4 have shown that when eco-cement was carbonation activated, the CE content was reduced and the $CaC0_3$, amorphous content, and gypsum was increased.

On the other hand, Concrete is the second most consumed material and cement industry is one of the largest contributors to the CO_2 emission in the world. Sustainability issues increased the importance of belite based cement, as these are more sustainable than ordinary Portland cement

(OPC) because these cements are produced at a lower temperature and emit lesser CO_2 [15] [16, 17]. Hydraulic reactivity of belite is lower as compared to the alite, that is why it has been considered as undesirable components of OPC. In contrast, belite showed high reactivity to CO_2 [18-20]. As already mentioned, due to low hydraulic behavior the hardening and strength developments of belite base cements requires accelerated carbonation, and the strength of these cement binders are analogous to 28 days hydrated strength of OPC [15, 21]. These binders showed CO_2 storing capacity up to 17 % of the mass of the binder during accelerated carbonation.

Researchers studied the effect of accelerated carbonation for hydraulic and non-hydraulic di-calcium silicates, they correlated the swift development of C-S-H to the rapid strength development of these binders and the possible carbonation reaction is presented in Equation 5.1 [20, 22]

$$2\,(2CaO.SiO_2) + CO_2 + 3H_2O \rightarrow 3CaO.\ 2SiO_2\ .3H_2O + CaCO_3 \qquad (5.1)$$

Carbonation of calcium-silicate system is a sequence of reactions, starting from the formation of carbonic acid from the hydration of CO_2 which drops the pH of the solution. Dissolution of calcium silicates accelerated in this low pH solution and SiO_4^{2-} and Ca^{2+} ions are released. These ions recombine and nucleates the C-S-H and calcium carbonate at the same time due to the thermodynamic conditions. Most of the reactions befall in aqueous solution, so the hydration is crucial to affluence the carbonation reaction [23].

Carbonation of calcium-silicate system also produces calcium carbonate. This process comprises a multi-step progression, ensuring a precipitation-dissolution-precipitation sequence [24, 25]. $CaCO^{3-}$hexahydrate, $CaCO^{3-}$monohydrate, and amorphous carbonate (ACC) are the main hydrous species defined by the researcher [26-28]. Calcium carbonate could be found in one of the three well known anhydrous polymorphs i.e. Aragonite, vaterite, and calcite. Favorable conditions transmute the thermodynamically unstable polymorphs (veterite and aragonite) to the calcite which is the most thermodynamically stable polymorph [29-31]. The absence of water could pause the progression of polymer evolution because a suitable amount of water is indispensable for the steady evolution [24, 32]. The stabilization of polymorphs is not very well understood, as many factors including temperature, water content and the presence of impurities could affect the polymorph development [27, 32, 33].

To understand the carbonation reaction of eco-cement and its strength development mechanism, this chapter will synthesize the CE and belite compounds will perform carbonation activation of CE, belite and their combination. The microstructure of carbonated CE, belite and their combination will be characterized by TG, QXRD, and SEM which will ultimately lead towards the better understanding of rapid strength mechanism of eco-cement. Furthermore, it will also help to rationalize the hypothesis presented in Chapter 4, which suggests the formation of amorphous calcium silicate hydrocarbonate, as a modified C-S-H by carbonate and the mechanism of strength development of eco-cement. It is hoped that this work will help advance the knowledge on carbonation activation of synthesized CE and belite as well as their combination and promote the application of eco-cement made from 94% MSWI residues.

5.3. MATERIALS AND METHODOLOGY

5.3.1. MATERIALS

5.3.1.1. PRODUCTION OF SYNTHESIZED CE

Chlorellestadite, with the ideal formula $Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$, was prepared by calcining stoichiometric amounts of CaO, SiO_2, $CaCl_2$, and $CaSO_4$. All the chemicals used were laboratory grade with a purity level of more than 99 %. All these compounds were mixed in acetone and then dried, after which the mixture was poured into an alumina boat and heated at 11000 °C. CE could be produced at 1000 °C, but to simulate the production conditions of eco-cement the temperature was raised to 1100°C and maintained for one hour. After one hour of calcining, the material was left inside the furnace for slow cooling. It took more than twelve hours to achieve room temperature. After that, the material was washed with water to remove excess $CaCl_2$ and analyzed by scanning electron microscopy (SEM) and X-Ray diffraction (XRD).

5.3.1.2. PRODUCTION OF SYNTHESIZED BELITE

Belite (Ca_2SiO_4) was synthesized by calcining the stoichiometric amounts of CaO and SiO_2 at CaO/SiO_2 ratio of 2/1. The chemical used for the synthesis were laboratory grade with a purity level of 99 %. The chemicals were mixed in acetone to achieve the homogeneous mixture, after that, it was dried at 60°C. The dried mixture was poured into an aluminum boat and fired at 1100°C for one hour to simulate the eco-cement production conditions. After one hour of calcination, the material was left inside the furnace for slow cooling. Slow cooling took approximately twelve hours to reach to the room temperature. The material was taken out of the furnace and examined by SEM and XRD to ensure and confirm the degree of purity of the synthesized product.

5.3.2. CARBONATION AND COMPRESSIVE STRENGTH TESTING

To study the microstructure of synthesized compounds, CE and belite paste samples were prepared by mixing 100 g synthesized powders with 9.5 g of water (water to cement ratio was 0.095) in a regular kitchen aid mixer. After the CE or belite and water were mixed at a lower speed for 1 minute, the material on the blade and sides were scrapped off and mixing process was continued for 30 seconds. Final mixing was carried out in three steps, mixing at medium speed for 1 minute, mixing at high speed for 30 seconds and lastly for 30 seconds at medium speed. The paste was compacted into small cylindrical compacts of 15 mm diameter and 30 mm length by keeping the aspect ratio of 2. For this purpose, MTS- SINTECH 30/G compressive tester equipped with 150 KN load cell machine was used, and maximum consolidation pressure of 5 MPa was applied. Carbonation curing was performed in a custom-built carbonation chamber using 99.5 % pure CO_2 at a pressure of 1.5 bar. The samples were carbonation cured for 2-hrs and 12-hrs based on the strength development of eco-cement.

To calculate the CO_2 uptake, the mass of cylindrical compacts was measured before and after the carbonation. Using the mass gain during the carbonation and the initial mass of the compacts, the net CO_2 uptake was calculated. For compressive strength measurements, the cylindrical compacts were tested for compressive testing in accordance with ASTM C-39 using MTS- SINTECH machine.

5.3.3. X-RAY DIFFRACTION MEASUREMENTS

To identify the purity of synthesized phases formed and their relative weight percentages were measured by means of QXRD. The Quantitative X-ray diffraction (QXRD) patterns of the synthesized powders and paste of CE and belite were recorded with Cu Kα radiation on a Siemens D-500 diffractometer. The diffraction pattern was obtained for the range of 2θ angles from 10° to 90° using the step size of 0.02. Cylindrical compacts prepared and cured as discussed in section 5.3.2 were ground into powder form to perform QXRD analysis.

5.3.4. THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA was conducted to determine the composition of synthesized phases and to predict their thermal stability. For the TGA, the carbonated paste samples were crushed manually and then sieved through number 200 sieve (0.074 mm opening). Commercially available instrument (TA instrument TGA Q500) was used to perform the TGA test. The powdered sample was first kept in isothermal condition for 10 min and then the temperature was raised at the rate of 10°C per minute up to 1000°C. Approximately 5 to 10 mg of powder samples were tested. Helium was used as purge gas during TGA tests.

5.3.5. SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

SEM was used to study the morphology of the samples and EDS was performed to identify the elements present in the phases. The SEM analysis was performed on cylindrical paste specimens. These compacts were randomly broken, a small piece from the broken surface was taken and nano-meter coating of platinum was applied to avoid the charging effect at high magnifications. Once prepared, the specimens were investigated using a scanning electron microscope (SEM) equipped with the energy dispersive X-ray (EDX) spectrometer operated either in the backscattered electron (BSE) or the secondary electron (SE) modes, depending on the type of examinations performed.

The SEM images and the EDX were obtained by FEI Inspect F50 Field Emission Scanning Electron Microscope (FESEM) operating in high vacuum mode with an accelerating voltage of 15 kV and using the working distance of 10.00 mm. Along with the SE images collected at different magnification levels, the EDX spectra were also acquired from selected individual points to perform the quantitative X-ray microanalysis. The energy-dispersive spectrometer measures the number and the energy of the X-rays emitted from a specimen. The energies of the X-rays are characteristic of the given chemical element and thus EDS allows for the determination of the elemental composition of the specimen.

5.4. RESULTS AND DISCUSSIONS

5.4.1. COMPRESSIVE STRENGTH AND CO_2 UPTAKE RESULTS

To understand the strength development and the microstructure of the synthesized CE and belite, the samples were divided into three categories; synthesized CE, synthesized belite and the mixture of CE and belite at a mass ratio of 3:1 to simulate the eco-cement composition. The CE: belite ratio in different batches were observed in the range of 2.5:1 to 4.5:1 with an average of 3:1. So, the CE and belite were mixed with a ratio of 3:1 for this study. The compressive strength results of synthesized compounds were compared with the strength of eco-cement. Compressive strength results and CO_2 uptake results are presented in Fig. 5.1. The average compressive strength of the synthesized CE compacts after 2-hours of carbonation was measured about 12 MPa and average CO_2 uptake was 3%. The average compressive strength and CO_2 uptake after twelve hours were doubled and recorded at about 25MPa and 6 % respectively. The same phenomenon was observed in the case of synthesized belite: the compressive strength jumped from 25 MPa to 45 MPa after two and twelve hours of carbonation respectively. The CO_2 uptake of belite was observed relatively high as compared to CE and eco-cement i.e. about 10% after two hours carbonation and 15 % after twelve hours carbonation curing. Synthesized CE and belite were mixed together in a 3:1 ratio to simulate the percentages observed in eco-cement. The results were quite interesting, as the compressive strength of mixed compounds after both carbonation times were higher than the individual compounds, the strength was even higher than the summation of compressive strength of individual compounds. The compressive strength of mixed compounds was observed as 52 MPa and 80 MPa after two and twelve hours of accelerated carbonation respectively. On the other hand, the algebraic sum of individual compressive strength of CE and belite was 37 MPa (12+25) and 70 MPa (25+45) after two and twelve hours of carbonation respectively. It was observed from Fig.

5.1 that the compressive strength of combined synthesized compounds was comparable to the compressive strength of the eco-cement for both curing durations. Compressive strength results helped to conclude that both compounds reacted better in combination and contributed more towards the strength. Furthermore, the control cylindrical samples were also tested after two and twelve hours to perceive the hydraulic reactivity of these compounds. The compressive strength of less than 1 MPa was measured after two- and twelve-hours hydration for all the synthesized samples and for the eco-cement as well. This confirmed the non-hydraulic or latent hydraulic performance of all the synthesized compounds and eco-cement as well.

5.4.2. QUANTITATIVE X-RAY DIFFRACTION (QXRD) ANALYSIS RESULTS

QXRD analysis results of synthesized compounds and eco-cement before and after carbonation are presented in Table 5.1 and 5.2 respectively. QXRD results confirmed the level of purity was 80% in synthesized CE and about 93 % in the case of synthesized belite. The synthesized compounds with this level of purity in a laboratory work were satisfactory. There were three other phases in a small amount that were produced during the synthesis of CE, which remain un-reacted during carbonation. When CE was exposed to carbonation curing, it reacted with CO_2 and produced calcium carbonate and gypsum, as well as the amorphous phase. Amorphous phase could be purely amorphous or could be some phase with a very low crystalline structure that could not be detected by XRD. The reaction rate was increased with the increase in carbonation duration i.e. the percentage of reaction products was increased, and the amount of unreacted CE was decreased after twelve hours of carbonation in comparison to two hours carbonation. On the other hand, when belite was exposed to carbonation, the major reaction products were calcium carbonate and amorphous phases. In the case of pure belite, the amorphous phase would be a form of calcium silicate hydrate. The effect of carbonation duration on reaction products was also observed in synthesized belite. The reaction products were higher after twelve hours carbonation in comparison to that of two hours carbonation. After the discrete carbonation of synthesized CE and belite, both compounds were mixed together, and carbonation was carried out for a duration of two and twelve hours. The relation between the carbonation reaction and the carbonation duration was observed analogous to the relation found during carbonation of individual synthesized compounds. Carbonation of mixed synthesized compounds formed the combination of reaction products of both individual compounds i.e. $CaCO_3$, gypsum and an increase in the amorphous phase. The QXRD of eco-cement is presented in Table 5.2, the comparison was drawn between the carbonation reaction of eco-cement and the mixture of synthesized CE and belite. The overall reaction was observed to be similar, but the amount of reaction products in eco-cement was in smaller quantities as compared to the synthesized mixture. This was explicable, as the eco-cement had other impurities/phases, and those phases decreased the overall carbonation reaction of eco-cement. Contrary to that, synthesized phases had a higher concentration of pure phases and carbonation reaction was not resisted by any impurities. In conclusion, it was observed that the binding matrix which is responsible for the high strength probably due to the combination of $CaCO_3$, gypsum and amorphous Ca-Si intermix (C-S-H-like phase).

5.4.3. THERMOGRAVIMETRIC TEST RESULTS

The thermogravimetric (TG) curves for the eco-cement paste, individually synthesized CE and belite, as well as the mixture compound, are presented in Fig. 5.2-5.5. It was observed that synthesized phases were quite stable, minimal mass loss (less than 3 %) was measured in individual and mixed synthesized compounds as well. In the case of carbonated synthesized samples, the mass loss in the temperature region of 500°C to 700°C is attributed to the decomposition of $CaCO_3$. The mass loss at the temperature of 100°C indicated the loss of physically and chemically bound water present in the gel phases. The mass loss at 110°C confirmed the presence of gypsum in case of CE individually and when mixed with belite, belite did not show any peak around 110°C. Synthesized pure phases almost stabilized after 800°C, especially belite. The TG curve of mixed synthesized compounds was analogous to the TG curve of eco-cement up to 800°C, that confirmed the presence of $CaCO_3$, Gypsum and calcium silicate hydrates. There is another drop that was observed in eco-cement after 800°C. Initially, it was believed to be the decomposition of CE but synthesized curved showed that the CE was almost stable after 800°C. The mass loss in eco-cement after the 800°C was due to some other impurities present, that need further investigation by coupling MS with TG. The mass losses in the synthesized compounds were higher than the eco-cement, that was expected as the eco-cement also had about 40% other phases.

5.4.4. SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

Micrographs of synthesized CE are presented in Fig. 5.6; unreacted, two hours carbonated, and twelve hours of carbonated are presented in Fig. 5.6(a), 5.6(b) and 5.6(c) respectively. The hexagonal rod-like crystals of unreacted CE was observed and those were confirmed by EDS. EC has needle-like hexagonal crystals as described by S. J. Saint-Jean et. al. during their research on the presence of CE in the preheat system of cement kilns [14]. From the SEM micrographs, it was observed that the carbonation time increases the reactivity and produced more compact microstructure. More unreactive crystals were observed in the micrographs of two hours carbonated sample as compared to the twelve hours of carbonated samples. Furthermore, it was also observed that the twelve hours carbonation physically increases the cohesion and compactness and reduced the porosity. The EDS of unreacted crystals available in all the samples showed the presence of all the main constituent element i.e. Cl, Si, SO and Cl (spot “B” of Fig. 5.6(a) and5.6 (b)). On the other hand, the reaction of EC with CO_2 changed the elemental composition, which was responsible for the production of carbonate modified calcium silicate hydrates (Calcium silicate hydrocarbonate), as the main elements detected in EDS were silicates and calcium with some amount of carbon (spot "A" Fig. 5.6(b) and 5.6(c)). SEM images of synthesized belite are presented in Fig. 5.7. It was observed from the micrographs that the unreacted belite crystals were bigger and prominent (Fig. 5.7 (a)). But reaction with CO_2 converted these crystals into the compact, dense and amorphous like material which could be observed from Fig. 5.7 (b) and 5.7(c). To simulate the eco-cement, CE and belite were mixed and carbonated. Micrographs of mixed material and eco-cement are presented in Fig. 5.8 and Fig. 5.9 respectively. The microstructure of eco-cement was found to be denser and compact as compared to the microstructure of synthesized mix compounds. It could be due to the presence of other unreacted phases in eco-cement, such as the impurities/unreacted compounds as fillers. On the other hand, the microstructure on synthesized mixed compounds (Fig. 5.8) was slightly porous and less dense, but the reactivity of the crystals was higher and reaction products were very visible and well grown (Fig. 5.8). The reason for the packed microstructure could be the availability of space to expand in all the directions due to the absence of impurities. The physical appearance of the mixed synthesized material microstructure was observed to be denser than the microstructures of individually synthesized compounds. This increase in density and reduction of porosity of mixed material could be the first reason of higher compressive strength, mechanical interlocking between the reaction products of carboned CE and belite was assumed to be the secondary contribution to the strength gain. Unreacted crystals of Belite and CE can be observed in spot "A" and spot "B" of Fig. 5.8 (a) respectively. From EDX presented in Fig. 5.8, it was observed that carbonation of CE and belite mixture produced amorphous calcium silicate hydrocarboante modified by Cl and S (spot "A" and "C" of Fig.5.8(b)), as well as crystalline phase of $CaCO_3$ (spot "B" Fig. 5.8(b)) and gypsum (spot

"B" Fig. 5.8(c)). The strength gain was attributed primarily to the chemical reaction, and secondarily to the frictional interlocking provided by reaction products of CE. Eco-cement micrographs are presented in Fig. 5.9, unreacted CE crystal and complex crestline phase of calcium-aluminum-sodium-chloride can be observed in the EDS spot "A" and "B" respectively. Gypsum can be seen in the spot "B" of Fig. 5.9(c), and the calcium silicate hydrocarbonate phase can be observed in the EDX spot "B" of Fig. 5.9(b) and spot"A" of Fig. 5.9(c).

To relate the chemical compositions to microstructure morphology in carbonated CE and eco-cement, powder samples of CE and eco-cement were carbonated by twelve hours and examined at higher magnification with EDS. The CE and eco-cement powders were carbonated for twelve hours in loose form, rather than in compacts. Accelerated carbonation time of twelve hours was chosen based on the strength development mechanism because synthesized CE and eco-cement paste showed highest compressive strength after twelve hours of carbonation, which lead to the more reacted and stabilized microstructure. By carbonating the loose powders instead of compacts, it helped study the microstructure at higher magnifications. Fig. 5.10 represents the micrographs of twelve hours carbonated CE at different magnifications, from 10,000x to 200,000x. It was observed that the physical appearance of carbonated CE crystals seemed to be very smooth at lower magnifications, but higher magnifications showed that each CE crystal was converted into a new fibrillar spindle-shaped microstructure. These fibrillar spindle-shaped microstructural phase was grown in multi-directions, and the shape of new microstructure showed micro-frictional points on the surface. The dimensions of these phases were in the range of nanometer to micrometers, the morphology of these shapes at higher magnification was analogous that very small particles in tens of nanometers were packed together, which could be quite similar to the packing model of C-S-H proposed by Jennings [34]. To study the elemental composition of the new microstructure resulted in the carbonation of CE crystals, EDS was carried out at higher magnification and presented in Fig. 5.11. EDS at higher magnification confirmed the presence of calcium and silicates in the fibrillar spindle-shaped reaction products of CE, which could be the indication of the formation of amorphous calcium silicate hydrocarbonate modified by Cl. SEM/EDS of eco-cement at higher magnification are presented in Fig. 5.12. It was observed that the same fibrillar spindle-shaped microstructure was found in eco-cement reaction products, but the size was smaller than that of synthesized CE microstructure. The size difference was logical, as in the synthesized CE the crystal had enough space to grow, but in the case of eco-cement, the growth was restricted by other unreacted phases. Moreover, the frictional interlocking between the fibrillar spindle-shaped microstructure and the amorphous phases was obvious and showed in Fig. 5.12 (a). At a magnification of 2000,000x (Fig. 5.12b), EDS result indicates that the produced amorphous phase was likely calcium silicate hydrocarbonate modified by Cl and S. In conclusion, compressive strength development of eco-cement was observed to be the result of the multifactored phenomenon. Carbonation products of CE and belite contributed to the strength development in term of formation of gypsum, calcium carbonate, and calcium silicate hydrocarbonate and by providing mechanical frictional interlocking at microstructure level.

5.5. CONCLUSIONS

In this research synthesized EC and belite were produced and carbonation activated for different durations. The microstructure was studied using different techniques and the conclusions are summarized below:

i. Carbonation curing duration enhanced the compressive strength of synthesized compounds either they were carbonated individually or carbonated in a mixture of two compounds. This observation confirms the longer carbonation time produces more reaction products and more compressive strength in eco-cement. This phenomenon was not observed in the OPC.

ii. A mix of synthesized CE and belite showed higher average compressive strength than the average compressive strength of individual synthesized components. It was also observed that the CE was a non-hydraulic material and belite showed negligible hydraulic properties at the early age of hydration.

iii. Carbonation curing for twelve hours had improved the microstructure as compared to two hours carbonated samples by decreasing physical porosity, growing the microstructure in all free spaces, producing denser microstructure and converting the maximum amount of CE into new phases.

iv. TGA confirmed the presence of calcium carbonate, gypsum, and calcium silicate hydrocarbonate in the carbonated synthesized CE and the in the mix of CE and belite. It was also observed that the synthesized compounds were almost stable after 800°C even after carbonation. Mass loss in eco-cement after 800°C was likely due to the decomposition of another unidentified phase.

v. SEM clearly showed the transformation of CE into another fibrillar spindle-shaped microstructure. EDS suggested that this phase likely to be amorphous calcium silicate hydrocarbonate, a C-S-H like a phase.

vi. The microstructure of eco-cement was analogous to the microstructure of synthesized mixed CE and belite, but the size of the reaction product was smaller than the size of synthesized mix reaction products. Presence of impurities/ unreacted phases in eco-cement could be the reason for this reduction in size and the amount of reaction products.

vii. It was observed from the compressive strength results and from the SEM micrographs, the superior binding strength developed in the matrix was the result of a combination of mechanical and chemical factors. Presence of calcium carbonate, modified C-S-H (calcium silicate hydrocarbonate) and gypsum chemically helped in strength development, and the hundreds of thousands fibrillar shaped friction points present on the modified microstructure of CE contributed to the strength gain mechanically.

REFERENCE

1. Hoornweg, D. and P. Bhada-Tata, *What a waste: a global review of solid waste management.* What A Waste: A Global Review of Solid Waste Management, 2012.
2. Stehlík, P., *Contribution to advances in waste-to-energy technologies.* Journal of Cleaner Production, 2009. **17**(10): p. 919-931.
3. Tang, J., R. Ylmén, M. Petranikova, C. Ekberg, and B.M. Steenari, *Comparative study of the application of traditional and novel extractants for the separation of metals from MSWI fly ash leachates.* Journal of Cleaner Production, 2018. **172**: p. 143-154.
4. Erol, M., S. Küçükbayrak, and A. Ersoy-Meriçboyu, *Production of glass-ceramics obtained from industrial wastes by means of controlled nucleation and crystallization.* Chemical Engineering Journal, 2007. **132**(1-3): p. 335-343.
5. Lederer, J., V. Trinkel, and J. Fellner, *Wide-scale utilization of MSWI fly ashes in cement production and its impact on average heavy metal contents in cements: The case of Austria.* Waste Management, 2017. **60**: p. 247-258.
6. Guo, X., H. Shi, W. Hu, and K. Wu, *Durability and microstructure of CSA cement-based materials from MSWI fly ash.* Cement and Concrete Composites, 2014. **46**: p. 26-31.
7. Shi, H.s., K. Deng, F. Yuan, and K. Wu, *Preparation of the saving-energy sulphoaluminate cement using MSWI fly ash.* Journal of Hazardous Materials, 2009. **169**(1-3): p. 551-555.
8. Saikia, N., S. Kato, and T. Kojima, *Production of cement clinkers from municipal solid waste incineration (MSWI) fly ash.* Waste Management, 2007. **27**(9): p. 1178-1189.
9. Shih, P.H., J.E. Chang, and L.C. Chiang, *Replacement of raw mix in cement production by municipal solid waste incineration ash.* Cement and Concrete Research, 2003. **33**(11): p. 1831-1836.
10. Wu, K., H. Shi, and X. Guo, *Utilization of municipal solid waste incineration fly ash for sulfoaluminate cement clinker production.* Waste Management, 2011. **31**(9-10): p. 2001-2008.
11. Ghouleh, Z. and Y. Shao, *Turning municipal solid waste incineration into a cleaner cement production.* Journal of Cleaner Production, 2018. **195**: p. 268-279.

12. Fang, Y.N., C. Ritter, and T.J. White, *Crystal chemical characteristics of ellestadite-type apatite: Implications for toxic metal immobilization.* Dalton Transactions, 2014. **43**(42): p. 16031-16043.

13. Rouse, R.C. and P.J. Dunn, *A contribution to the crystal chemistry of ellestadite and the silicate sulfate apatites.* American Mineralogist, 1982. **67**(1-2): p. 90-96.

14. Saint-Jean, S.J., E. Jøns, N. Lundgaard, and S. Hansen, *Chlorellestadite in the preheater system of cement kilns as an indicator of HCl formation.* Cement and Concrete Research, 2005. **35**(3): p. 431-437.

15. Ashraf, W., J. Olek, and J. Jain, *Microscopic features of non-hydraulic calcium silicate cement paste and mortar.* Cement and Concrete Research, 2017. **100**: p. 361-372.

16. Development, W.B.C.f.S., *Cement Technology Roadmap 2009: Carbon Emissions Reductions Up to 2050*. 2009.

17. Scalenghe, R., F. Malucelli, F. Ungaro, L. Perazzone, N. Filippi, and A.C. Edwards, *Influence of 150 years of land use on anthropogenic and natural carbon stocks in emilia-romagna region (Italy).* Environmental Science and Technology, 2011. **45**(12): p. 5112-5117.

18. Berger, R.L., J.F. Young, and K. Leung, *Acceleration of hydration of calcium silicates by carbon dioxide treatment.* Nature Physical Science, 1972. **240**(97): p. 16-18.

19. Ashraf, W. and J. Olek, *Carbonation behavior of hydraulic and non-hydraulic calcium silicates: potential of utilizing low-lime calcium silicates in cement-based materials.* Journal of Materials Science, 2016. **51**(13): p. 6173-6191.

20. Bukowski, J.M. and R.L. Berger, *Reactivity and strength development of CO2 activated non-hydraulic calcium silicates.* Cement and Concrete Research, 1979. **9**(1): p. 57-68.

21. Qian, B., X. Li, and X. Shen, *Preparation and accelerated carbonation of low temperature sintered clinker with low Ca/Si ratio.* Journal of Cleaner Production, 2016. **120**: p. 249-259.

22. Young, J.F., R.L. Berger, and J. Breese, *Accelerated Curing of Compacted Calcium Silicate Mortars on Exposure to CO<inf>2</inf>.* Journal of the American Ceramic Society, 1974. **57**(9): p. 394-397.

23. Fernández Bertos, M., S.J.R. Simons, C.D. Hills, and P.J. Carey, *A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2.* Journal of Hazardous Materials, 2004. **112**(3): p. 193-205.

24. Gal, J.-Y., Y. Fovet, and N. Gache, *Mechanisms of scale formation and carbon dioxide partial pressure influence. Part I. Elaboration of an experimental method and a scaling model.* Water Research, 2002. **36**(3): p. 755-763.

25. Gal, J.Y., Y. Fovet, and N. Gache, *Mechanisms of scale formation and carbon dioxide partial pressure influence. Part II. Application in the study of mineral waters of reference.* Water Research, 2002. **36**(3): p. 764-773.

26. Hu, Q., J. Zhang, H. Teng, and U. Becker, *Growth process and crystallographic properties of ammonia-induced vaterite.* American Mineralogist, 2012. **97**(8-9): p. 1437-1445.

27. López-Arce, P., L.S. Gómez-Villalba, S. Martínez-Ramírez, M. Álvarez de Buergo, and R. Fort, *Influence of relative humidity on the carbonation of calcium hydroxide nanoparticles and the formation of calcium carbonate polymorphs.* Powder Technology, 2011. **205**(1): p. 263-269.

28. Liu, C.Z., C.H. Lin, M.S. Yeh, Y.M. Chao, and P. Shen, *Surface Modification and Planar Defects of Calcium Carbonates by Magnetic Water Treatment.* Nanoscale Research Letters, 2010. **5**(12): p. 1982.

29. Wehrmeister, U., D.E. Jacob, A.L. Soldati, N. Loges, T. Häger, and W. Hofmeister, *Amorphous, nanocrystalline and crystalline calcium carbonates in biological materials.* Journal of Raman Spectroscopy, 2011. **42**(5): p. 926-935.

30. Goto, S., K. Suenaga, T. Kado, and M. Fukuhara, *Calcium Silicate Carbonation Products.* Journal of the American Ceramic Society, 1995. **78**(11): p. 2867-2872.

31. Ni, M. and B.D. Ratner, *Differentiating calcium carbonate polymorphs by surface analysis techniques—an XPS and TOF-SIMS study.* Surface and Interface Analysis, 2008. **40**(10): p. 1356-1361.

32. Ogino, T., T. Suzuki, and K. Sawada, *The rate and mechanism of polymorphic transformation of calcium carbonate in water.* Journal of Crystal Growth, 1990. **100**(1): p. 159-167.

33. Briones, M.J.I., E. López, J. Méndez, J.B. Rodríguez, and L. Gago-Duport, *Biological control over the formation and storage of amorphous calcium carbonate by earthworms*, in *Mineralogical Magazine*. 2008. p. 227.

34. Jennings, H.M., *Refinements to colloid model of C-S-H in cement: CM-II.* Cement and Concrete Research, 2008. **38**(3): p. 275-289.

Table 5.1: Quantitative phase analysis of synthesized CE and belite after carbonation activation via QXRD

Compound Name	Formula	CE	CE 2h	CE 12h	Belite	Belite 2 h	Belite 12 h	CE+ Belite	CE+ Belite 2h	CE+ Belite 12h
CE	$Ca_{10}(SO_4)_3(SiO_4)3Cl_2$	79.8	57.3	43.5	n.d	n.d	n.d	61.6	45.2	36.6
Calcium Silicate Chloride	$Ca_{10}\,Si_6\,O_{21}\,Cl_2$	4.0	4.0	4.0	n.d	n.d	n.d	1.8	1.9	1.8
Wollastonite	$Ca\,SiO_3$	3.8	4.0	3.9	n.d	n.d	n.d	2.6	2.3	n.d
Belite	Ca_2SiO_4	n.d	n.d	n.d	92.4	62.3	52.6	23.5	14.5	9.3
Anhydrite	$CaSO_4$	4.2	4.1	4.2	n.d	n.d	n.d	2.2	2.5	2.1
Gypsum	$Ca\,SO_4.\,2H_2O$	n.d	6.4	6.8	n.d	n.d	n.d	n.d	4.7	6.7
Vaterite + Calcite	$Ca\,CO_3$	n.d	5.0	8.2	n.d	10.7	15.8	n.d	10.8	15.6
Amorphous	-	8.2	19.2	29.4	7.6	26	31.6	8.3	18.1	27.9

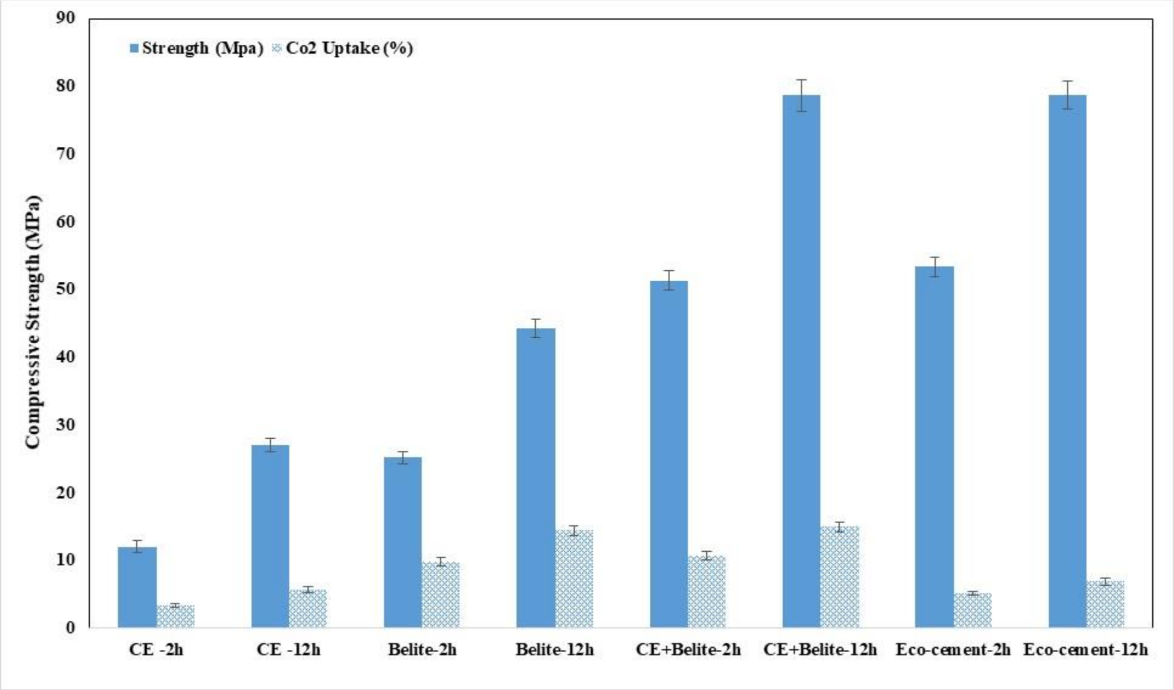
*2h: after 2 hours carbonation curing, 12h: after 12 hours carbonation curing

** n.d : Not Detected

Table 5.2: Quantitative phase analysis of eco-cement powder and after carbonation activation via QXRD

Compound	**Formula**	**Eco-cement**	**Eco-cement after 2h CO_2 activation (%)**	**Eco-cement after 12h CO_2 activation (%)**
Chloro-Ellestadite	$Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$	43.8	20.8	10.25
Wadalite	$Ca_6Al_5Si_2O_{16}Cl_3$	6.4	6.2	5.85
Bredigite	$Ca_7Mg(SiO_4)_4$	5.0	4.8	4.75
Quartz	SiO2	0.5	0.4	0.4
Halite	NaCl	2.9	2.0	1.95
Sylvite	KCl	1.4	0.9	1.0
Belite	Ca_2SiO_4	9.6	6.5	3.10
Gypsum	CaSO4.2(H2O)	n.d.	7.4	8.40
Vaterite	CaCO3	n.d.	4.2	6.20
X-Ray insensitive	Amorphous	30.4	46.8	58.1

**2h: after 2 hours carbonation curing, 12h: after 12 hours carbonation curing



**2h: after 2 hours carbonation curing, 12h: after 12 hours carbonation curing

FIGURE 5.1: COMPRESSIVE STRENGTH AND CARBON UPTAKE RESULTS

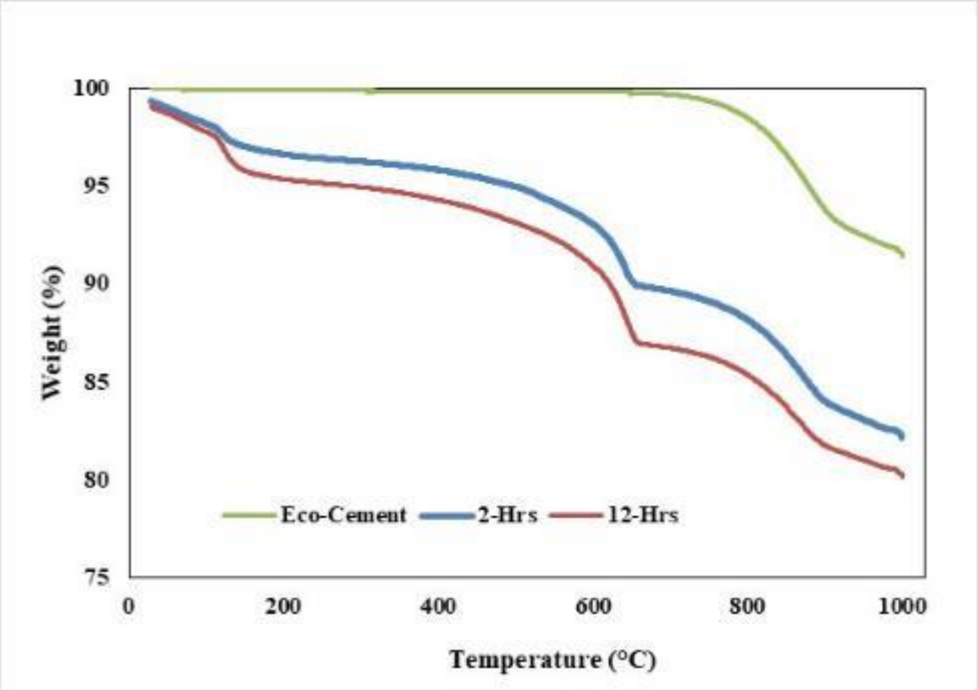


FIGURE 5.2: TGA CURVES FOR ECO-CEMENT BEFORE AND AFTER CARBONATION

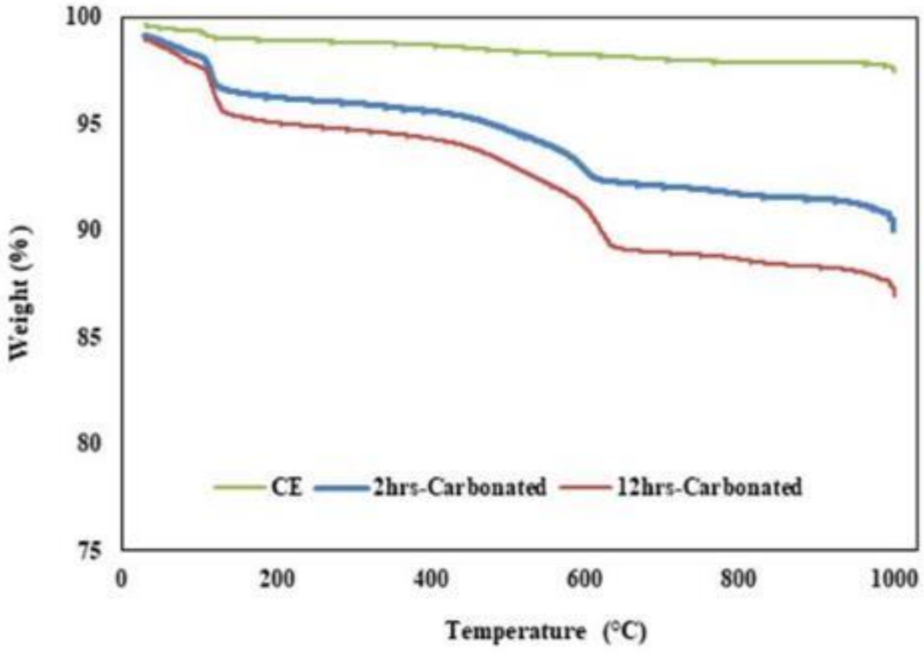


FIGURE 5.3: TGA CURVES FOR SYNTHESIZED CE BEFORE AND AFTER CARBONATION

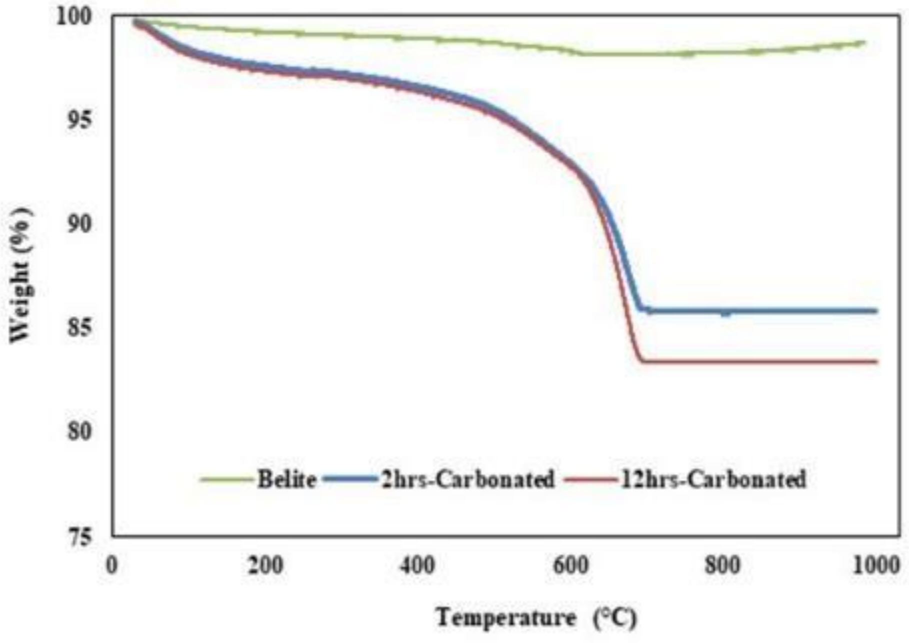


FIGURE 5.4: TGA CURVES FOR SYNTHESIZED BELITE BEFORE AND AFTER CARBONATION

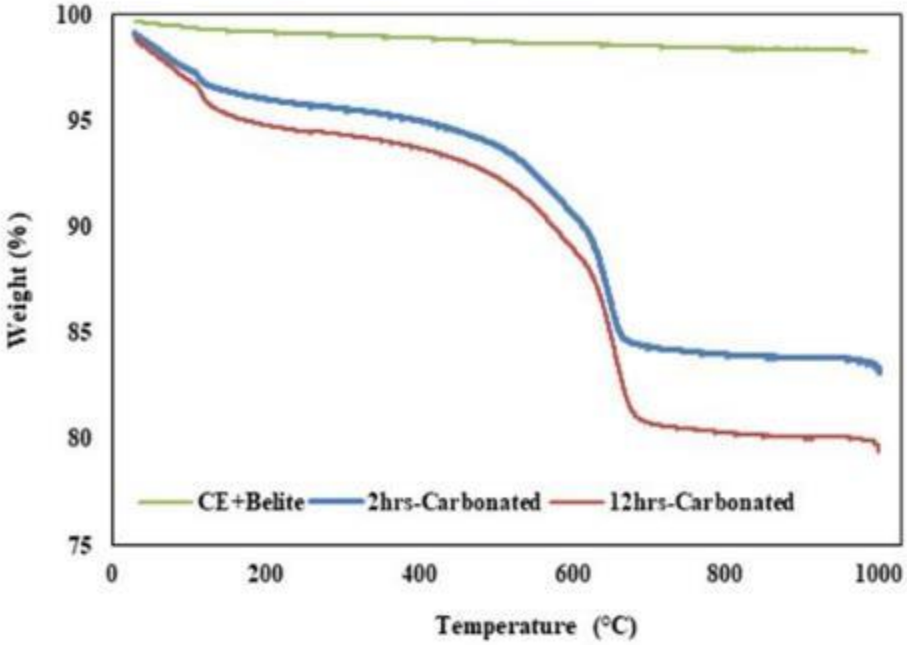
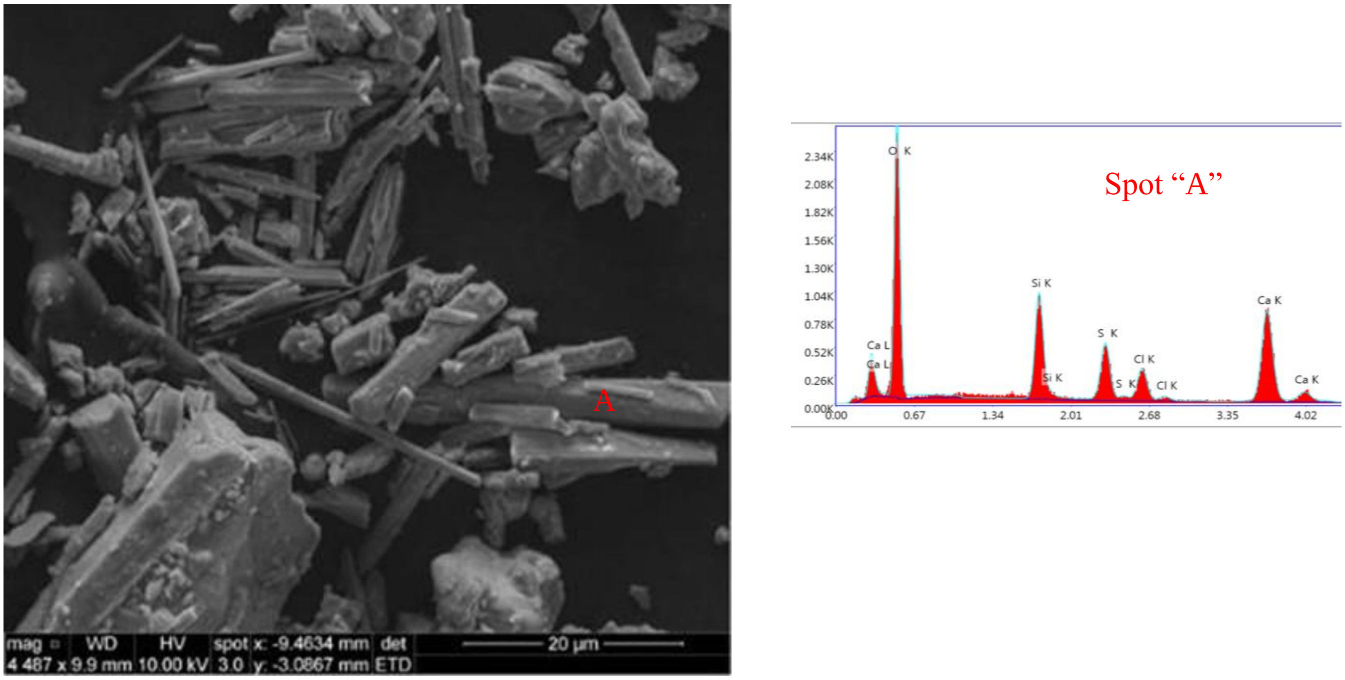
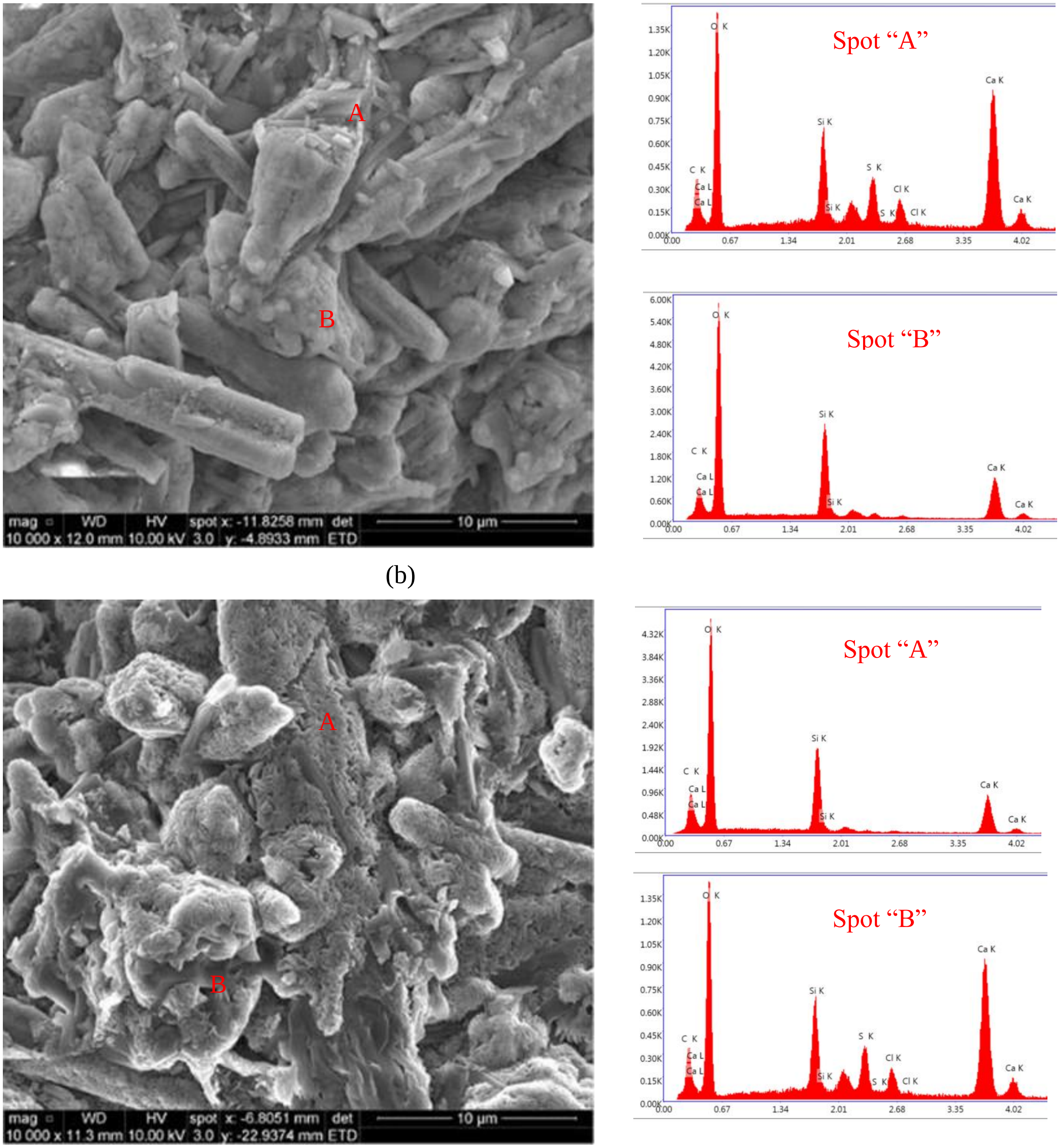


FIGURE 5.5: TGA CURVES FOR SYNTHESIZED CE+BELITE BEFORE AND AFTER CARBONATION



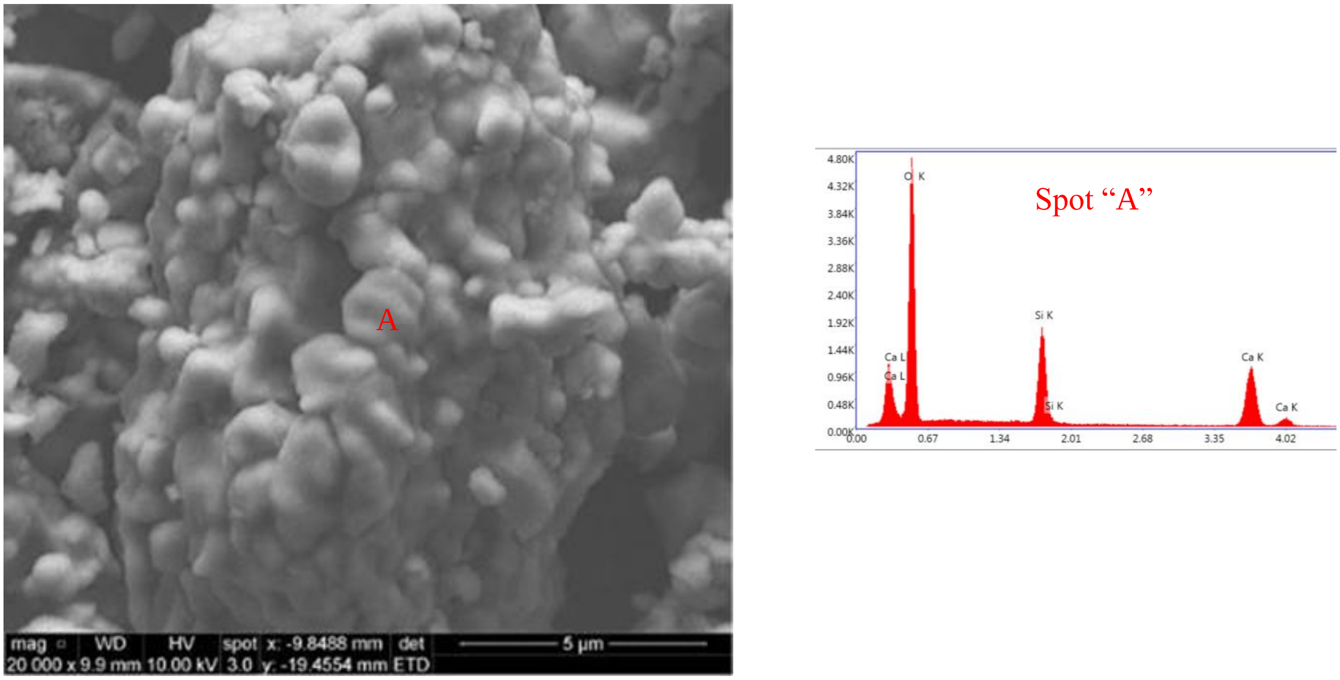
(a)



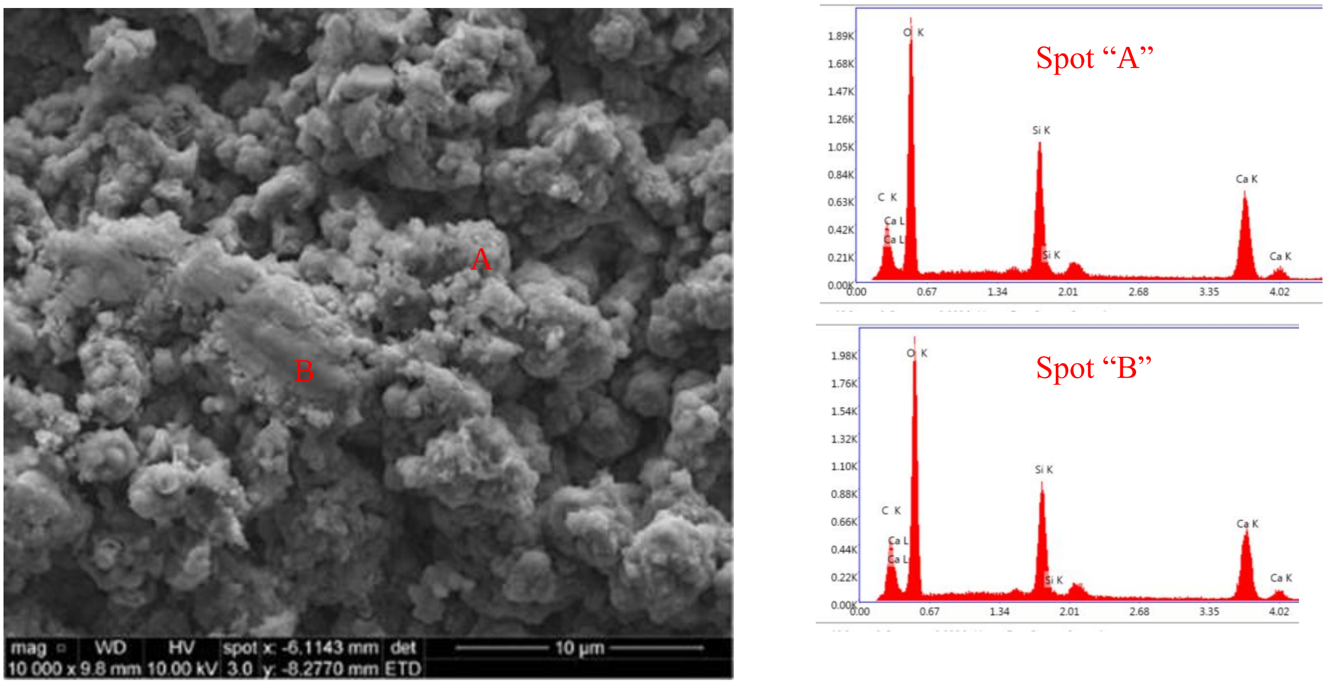
(b)

(c)

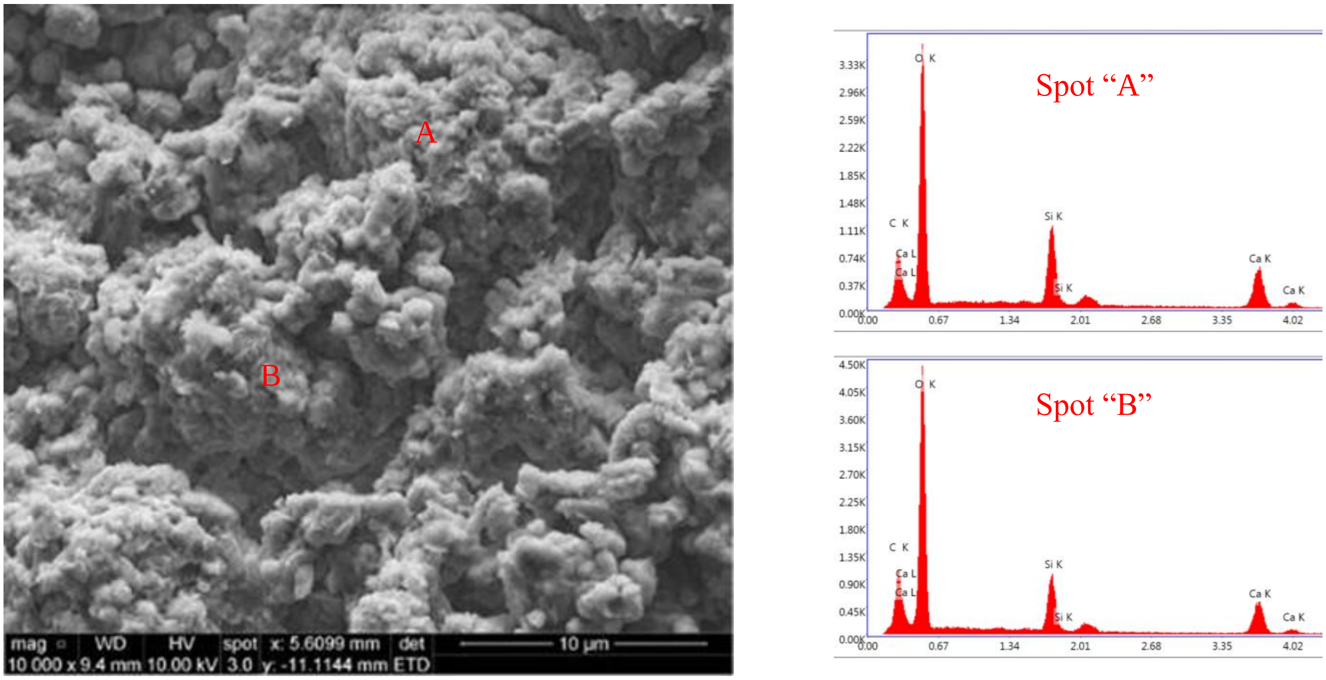
5.6: SEM/EDS OF SYNTHESIZED CE (A): POWDER (B): AFTER 2H CARBONATION CURING (C): AFTER 12H CARBONATION CURING


A
mag □ WD HV spot x: -9.8488 mm det
20 000 x 9.9 mm 10.00 kV 3.0 y: -19.4554 mm ETD
5 µm
Spot "A"
O K
Si K
Ca L
Ca L
Si K
Ca K
Ca K
4.80K
4.32K
3.84K
3.36K
2.88K
2.40K
1.92K
1.44K
0.96K
0.48K
0.00K
0.00
0.67
1.34
2.01
2.68
3.35
4.02

(a)

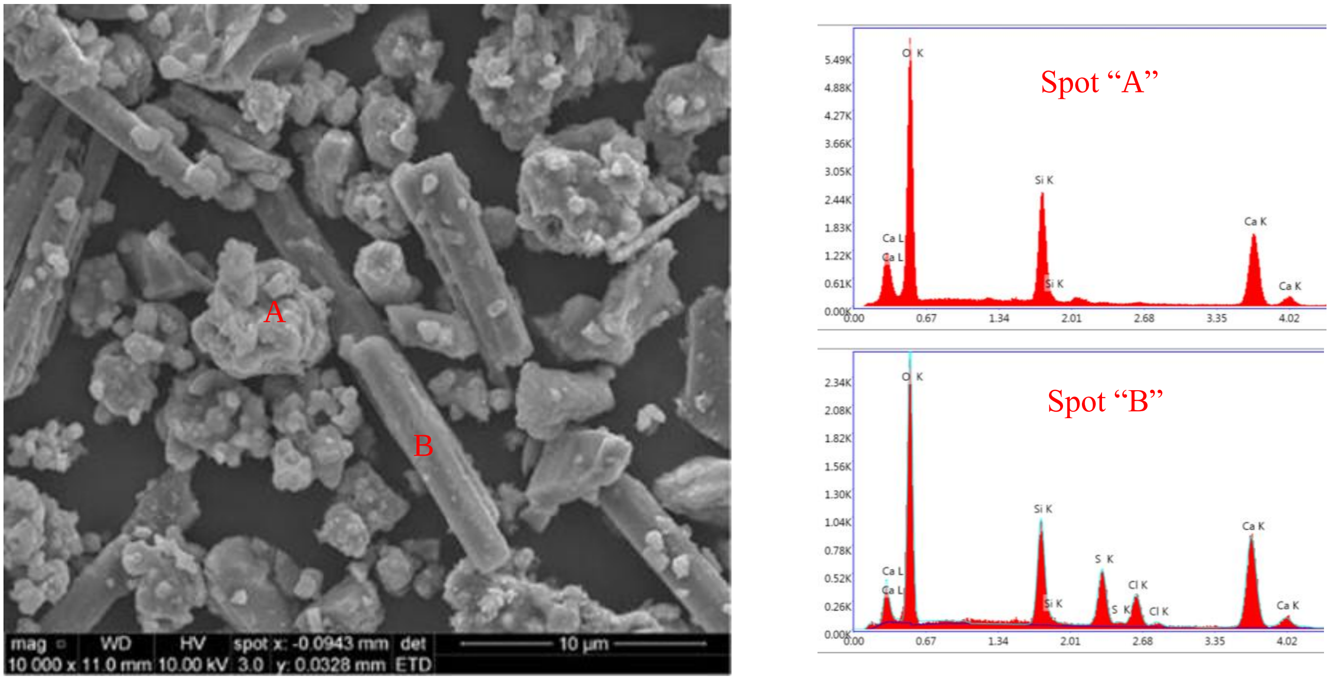

A
B
mag □ WD HV spot x: -6.1143 mm det
10 000 x 9.8 mm 10.00 kV 3.0 y: -8.2770 mm ETD
10 µm
Spot "A"
O K
Si K
C K
Ca L
Ca L
Si K
Ca K
Ca K
1.89K
1.68K
1.47K
1.26K
1.05K
0.84K
0.63K
0.42K
0.21K
0.00K
0.00
0.67
1.34
2.01
2.68
3.35
4.02
Spot "B"
O K
Si K
C K
Ca L
Ca L
Si K
Ca K
Ca K
1.98K
1.76K
1.54K
1.32K
1.10K
0.88K
0.66K
0.44K
0.22K
0.00K
0.00
0.67
1.34
2.01
2.68
3.35
4.02

(b)

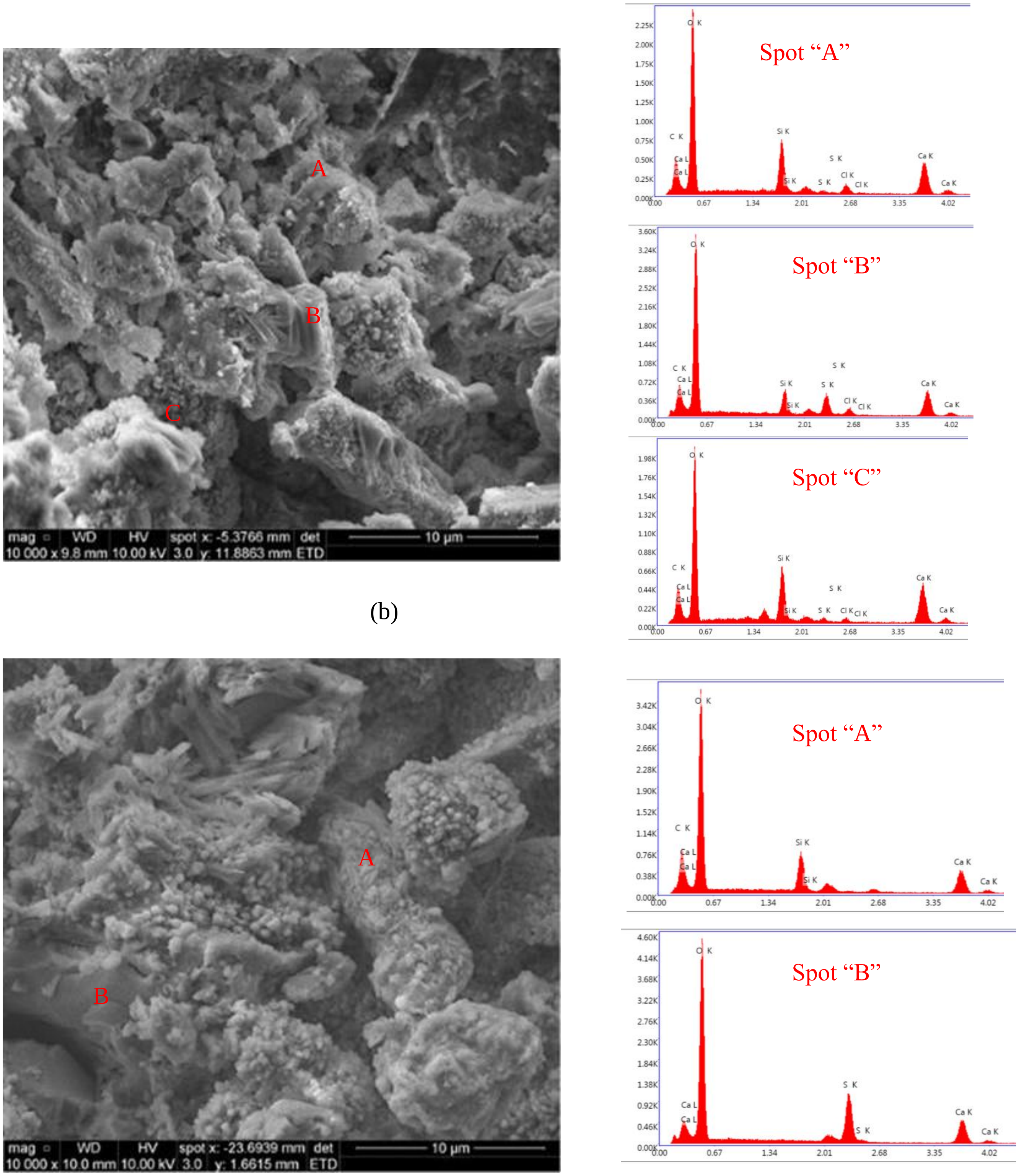


(c)

5.7: SEM/EDS of synthesized belite (a): Powder (b): After 2h carbonation curing (c): After 12h carbonation curing



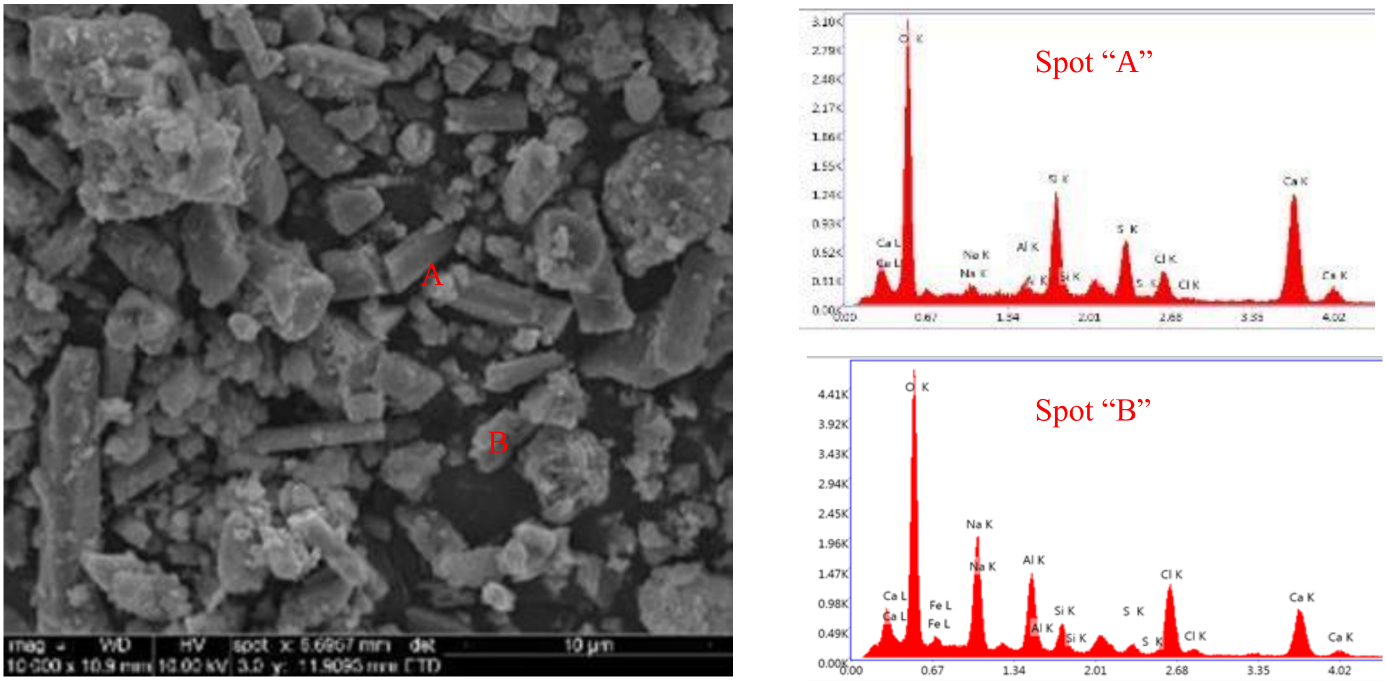
(a)



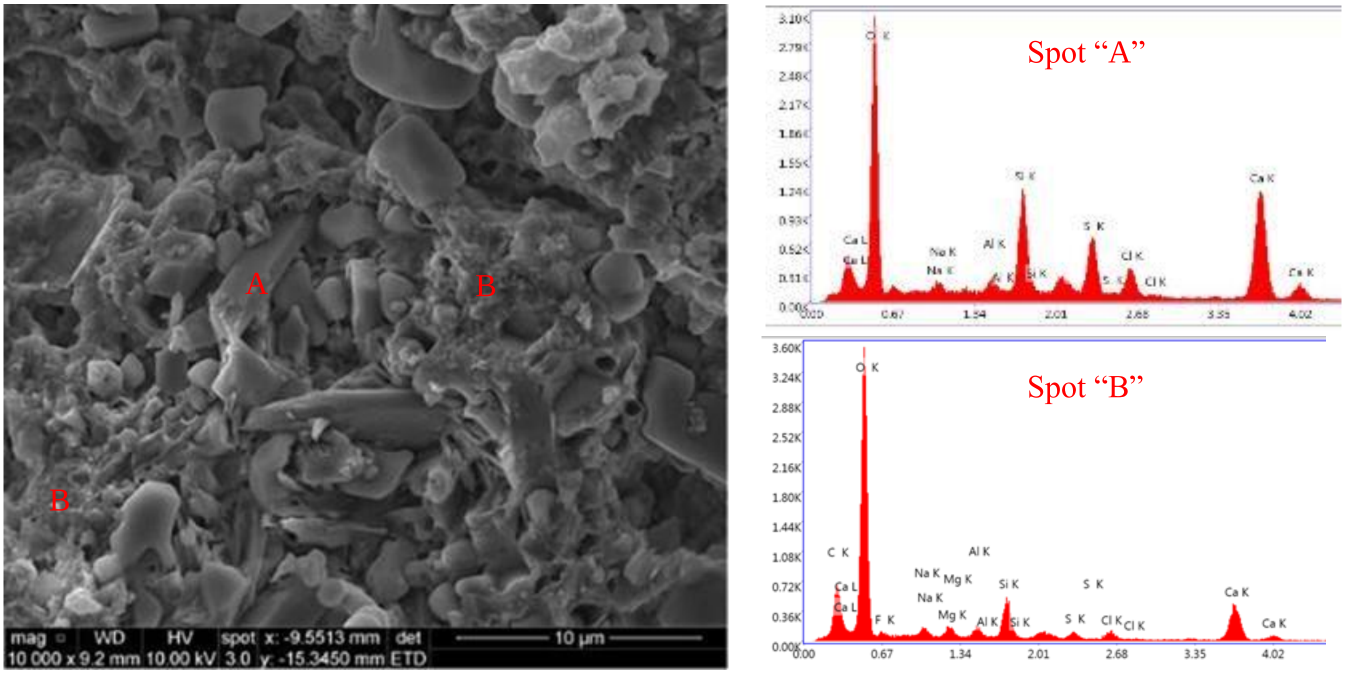
(b)

(c)

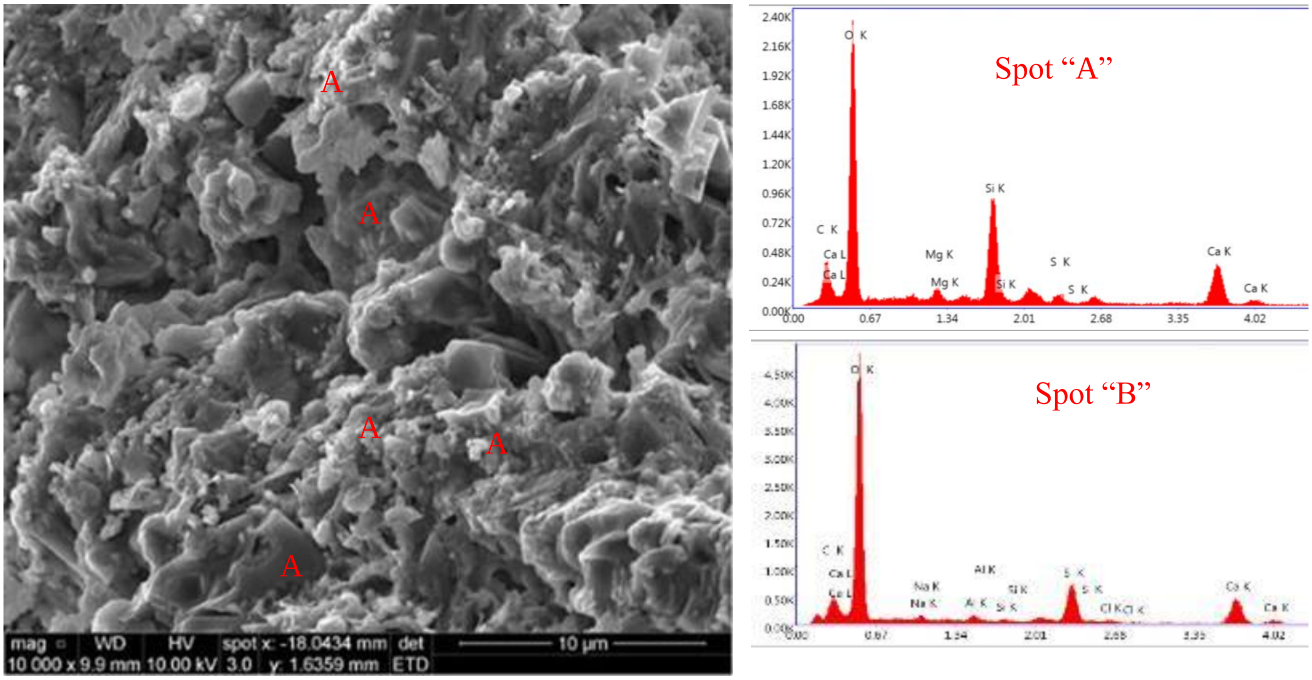
5.8: SEM/EDS OF SYNTHESIZED CE+BELITE (A): POWDER (B):AFTER 2H CARBONATION CURING (C): AFTER 12H CARBONATION CURING


A
B
mag WD HV spot x: 5.6967 mm det
10 000 x 10.9 mm 10.00 kV 3.0 y: 11.9095 mm ETD
10 μm
Spot "A"
O K
Si K
Ca K
S K
Cl K
Al K
Na K
Ca L
Spot "B"
O K
Na K
Al K
Cl K
Ca K
Si K
S K
Fe L
Ca L
0.00
0.67
1.34
2.01
2.68
3.35
4.02

(a)

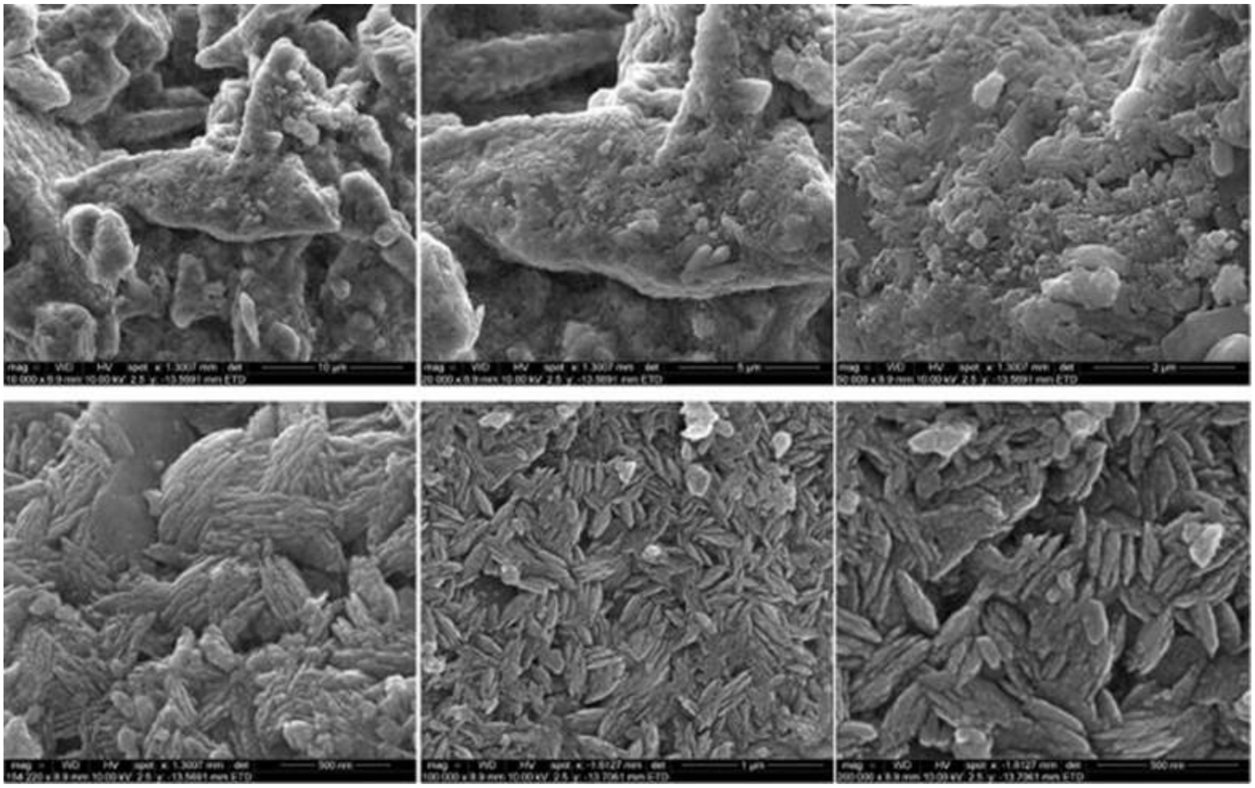

A
B
B
mag WD HV spot x: -9.5513 mm det
10 000 x 9.2 mm 10.00 kV 3.0 y: -15.3450 mm ETD
10 μm
Spot "A"
O K
Si K
Ca K
S K
Cl K
Al K
Na K
Ca L
Spot "B"
O K
C K
Ca L
F K
Na K
Mg K
Al K
Si K
S K
Cl K
Ca K
0.00
0.67
1.34
2.01
2.68
3.35
4.02

(b)

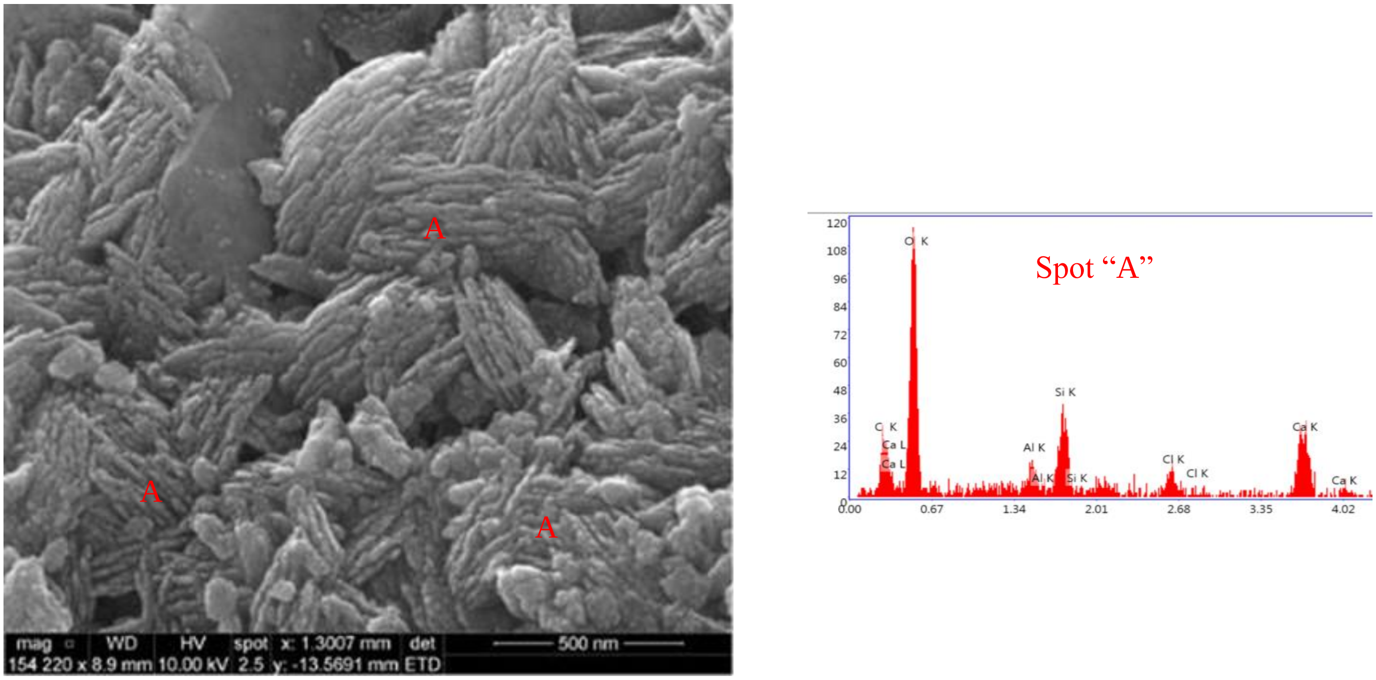


(c)

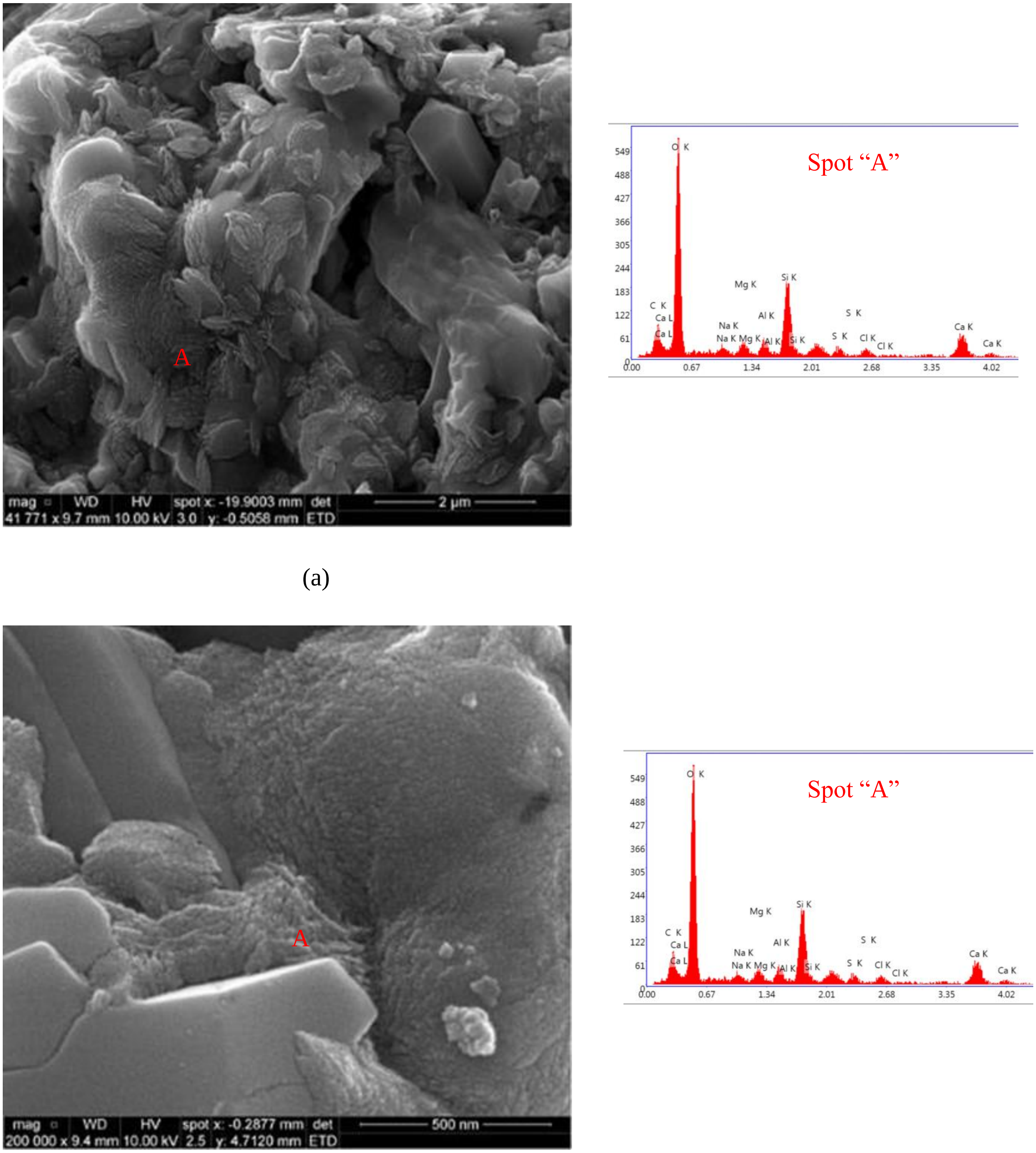
Figure 5.9: SEM/EDS of eco-cement (a): Eco-cement (b): After 2h carbonation curing (c): After 12h carbonation curing



5.10: SEM/EDS of 12hrs-carbonated synthesized CE paste



5.11: SEM/EDS of 12hrs-carbonated synthesized CE paste



(a)

(b)

FIGURE 5.12: SEM/EDS OF 12HRS-CARBONATED ECO-CEMENT PASTE (A) LOWER MAGNIFICATION (B) HIGHER MAGNIFICATION

CHAPTER 6. ENVIRONMENTAL IMPACT ASSESSMENT OF ECO-CEMENT MADE FROM MUNICIPAL SOLID WASTE INCINERATION RESIDUES

PREFACE

Production of eco-cement from the municipal solid waste incineration (MSWI) residues was discussed comprehensively in Chapter 3, and the characterization of the product was comprehensively discussed in Chapter 4 and Chapter 5. In Chapter 3, up to 94% of MSWI residues were used as a raw meal to produce eco-cement with a clinkering temperature of 1100°C. Eco-cement demonstrated non-hydraulic behavior and showed high reactivity with CO_2. Early age carbonation curing of two hours showed the compressive strength comparable to 28 days hydration strength of ordinary Portland cement (OPC). This increase in carbonation strength was more significant after extended carbonation of twelve hours. Development of eco-cement-based concrete was also demonstrated in previous chapters. The target product for the eco-cement concrete is concrete masonry block and non-reinforced precast members. Commercial use of eco-cement required an environmental assessment, as the eco-cement used MSWI residues as the raw meal for the production, and these residues contain toxic contaminations such as heavy metals, dioxin, and furans, etc. As discussed earlier, high-temperature clinkering is required for eco-cement production and carbonation curing is required to develop compressive strength. These processes could help immobilize the contaminants and improve the environmental acceptable criteria. This chapter is intended to study the effect of clinkering and carbonation on the environmental performance of eco-cement. To accomplish this objective, the extensive testing defined by EPA will be carried out on the raw meal, eco-cement, and carbonated eco-cement. In addition to the leaching testing, bulk testing will also be carried out to determine the total amount of contamination. The major contribution of this chapter is to provide evidence about the effect of clinkering and carbonation on the environmental performance of eco-cement. These results will help allow the safe use of eco-cement.

6.1 ABSTRACT

Eco-cement was derived from municipal solid waste incineration (MSWI) residues. MSWI residues are rich in hazardous materials such as heavy metals, dioxin, and furans. These materials could leach out from the cement and can contaminate the surrounding environment, leading to a health threat to humans. To address this issue, a comprehensive environmental impact assessment was conducted. To track the effect of clinkering and carbonation, the tests were performed on the materials at the different levels of production line i.e. raw blend before the clinkering, eco-cement after clinkering and eco-cement after the carbonation activation. The tests were performed on the extracted leachate of the material to simulate leaching conditions. To estimate the worst scenario, the total amount of hazardous materials was also measured using the bulk testing. From the results, it was observed that the clinkering process was able to immobilize most of the heavy metals, but few metals such as Chromium showed the inverse behavior. Carbonation activation fixed all the heavy metals effectively. The quantities of volatile organic compounds (VOC) and polycyclic aromatic hydrocarbons (PAH) were found under the detection limits. Dioxin and furans were destroyed by the clinkering process due to the elevated temperature and long detention time. Clinkering process and the carbonation activation Immobilized all the hazardous materials and made the eco-cement environmentally safe.

Keywords: Eco-cement, clinkering, carbonation activation, heavy metals, dioxin, and furans

6.2 INTRODUCTION

Every year billions of tons of municipal solid waste are generated. They are either landfilled or incinerated. In the developed countries where environmental protection laws are tight, and the availability of landfill sites are scarce, incineration is a widely chosen process [1, 2]. In Japan, about 80% of MSW is incinerated. However, in China, more than 80 % of the MSW is landfilled [3]. The incineration process could be divided into three major parts; incineration, energy recovery and air pollution control. The residues collected from incineration include bottom ash, boiler ash, and APC residues respectively, as described in Chapter 3 [4]. Recycling and reusing are the best strategies for MSWI residues management, even though these residues are rich in different contamination such as heavy metal, salts, and organic metals. These SMWI residues are being utilized in different ways in developed countries. In China, the MSWI residues were used to produce glass-ceramic, ceramic tiles and raw meal for the cement production [5]. MSWI residues were mostly used in the cement clinker production by the researchers in Japan and Taiwan [6, 7]. Spain utilized these residues as aggregates in concrete production and as a base in road construction [8]. In France and, Italy and Slovenia, MSWI residues were used as aggregates in concrete production [9]. Indians used the MSWI residues as an adsorbent for dyes [10]. The mineral composition of MSW varies from country to country, society to society and over time in the same society. The MSWI residues mineral composition depends on the raw composition of MSW [11]. The major elements of these MSWI residues are Ca, Si, Al, Fe, Mg, Cl, Na and K, and the common oxide found in these residues are CaO, SiO2, Na2O, K2O, Al2O3, and SiO2. The availability and amount of these minerals and oxides are subject to changes on the season and inhabitant. MSWI bottom ash is very rich in SiO2 and it could be up to the 50% of total ash contents and the APC residues contain CaO up to 46 % [7]. In addition to the valuable minerals and oxides, these MSWI residues also contain heavy metals, dioxin, and organic compounds as well. MSWI residues contain Cr, Cu, Hg, Cd, Zn, Ni, and Pb, usually, Pb and Zn exist in large volumes. Generally, fly ash contains higher amounts of metals and as compare to bottom ash due to the vaporization of metals during combustion [12]. MSWI bottom ashes contain a lesser amount of chlorine as compared to the MSWI fly ash. The presence of scrubber in the air pollution control system could be the reason, the acidic gasses such as HCl is removed by these scrubbers and causes in the increase of chlorine in APC residues. MSWI bottom ash has the loss on ignition 3-5% and fly ash showed a loss on ignition in the range of 4-13% [6, 13]. The international standards for dioxin emission in the flue gas is 0.1 ng I-TEQ/m3 (nano-gram International Toxic Equivalent/m^3). The dioxin-like compounds (DLC) is usually expressed in terms of toxic equivalence (TEQ), which is a product of available DLCs and their corresponding toxic equivalence factors (TEF). In other words, TEQ represents the toxicity of a combination of DLCs, when the toxicity value of each DLC is vague. In Japan ministry of environment limit for the dioxin levels in soils is 1 ng I-TEQ/g [14]. In most of the countries, the MSWI flash ash values cross the Japanese limiting values for dioxin. In China, the dioxin was found in the range from 0.798 to 7.53 ng I-TEQ/m3 [15]. In Korea and Taiwan, the dioxin was found as 0.13 I-TEQ/m3 and 0.47 I-TEQ/m3 respectively [15]. Activated carbon injections are used to adsorb dioxin and the lime scrubbers to remove the dioxin by changing the vapor phase to solid phase [14, 15]. Thus, the APC residues classified as hazardous waste as they contain relatively high amounts of dioxin [16]. The dioxin and furans formation could be reduced by different methods during the incineration of MSW. Proper combustion of MSW and the better designed APC are effective ways to control dioxin and furans. The production of dioxin will be minimized if the combustion of MSW takes place above 1000 °C and turbulence of combustion chamber is greater than a Reynold number of 50,000 and a resistance time more than 1 second. The reduction of formation or minimization of dioxin in the flue gas could be boosted by cooling the flue gas from 400 to 250 °C and lime scrubbers [17].

In order to reduce the environmental impact and utilize the MSWI residues, many methods are adopted. Thermal treatment and carbonation stabilization are commonly used methods after the separation and washing process [18]. The thermal process can decrease the toxic contamination and high temperature of 1400°C will effectively destroy the dioxin and furans [19]. Bottom ash could be used after the fusion and vitrification, and vitrification of APC residues recovered 100 % of toxic heavy metals and completely detoxified the residues [20]. The vitrified bottom ash showed lower leachability as compared to the original bottom ash. Although vitrification is very energy intensive and expensive, however, vitrification could be a sustainable option for MSWI residue treatment [21]. On the other hand, hazardous waste could be treated very effectively by the accelerated carbonation process. Carbonation of MSWI residues showed good results for stabilizing heavy metals especially lead and zinc [22]. The carbonation reduces the pH, porosity and pore area of the products. This reduction of pH helps immobilize heavy metals and toxic content of MSWI residues [23].

MSWI residues with the application of treatments could be used for different applications. Technical performance, environmental impact, and suitability of processing are the main factors to decide the possible applications [24]. MSWI residues showed a potential use in different industries such as glasses and ceramic industry, agriculture, wastewater treatment, zeolite production and widely in the construction industry. APC residues were used to synthesized zeolite by hydrothermal process. Higher concentration of heavy metals such as Zn and Pb were found in the residual liquid after the synthesis, therefore, further treatment was required before discharge

[25]. MSWI bottom ash was also used to synthesized zeolite, but this is less common than using APC residues for synthetization of zeolite [26]. Furthermore, MSWI bottom ash was successfully used as adsorbent and to remove heavy metals from wastewater [10]. Although MSWI bottom ash contains heavy metals and has leachability problems, due to higher toxicity of heavy metal, the presence of heavy metals in the water is more serious [27]. MSWI bottom ash was also used for purification of gas. Sulfur was reduced by using MSWI bottom ash from a landfill gas [28]. APC residues showed the potential to be used as an adsorbent for heavy metals, dyes and organics [29]. In addition, MSWI residues were used to produce glasses, ceramics, and glass-ceramics as they contain a high amount of SiO_2, CaO, and Al_2O_3. The ceramic tiles were produced by using MSWI ashes up to 20% showed high compressive strength and low absorption of water and vitrified MSWI residues used as raw material to produce glass-ceramics successfully [13]. Another direct and simple method of MSWI ashes is to replace the base course of roads widely [30, 31]. The MSWI ash stabilized by washing showed better results than the cement stabilized ashes used in the road base courses [32]. MSWI bottom ashes were also used as aggregates in roads and concrete construction [33]. APC residues were used successfully to produce lightweight aggregates [34]. Over and above, MSWI ashes are rich in SiO2, CaO, Fe2O3 and Al2O3, that is similar to the raw feed material of cement production. Thus, these residues could be used as a raw meal in the production of Portland cement. The MSWI residues were used up to 45% in the production of blended cement and up to 85% as a raw meal to produce clinkers as well [35] [7, 36].

The research reported in this thesis has developed eco-cement by using the MSWI residues up to 94% as a raw meal and at a clinkering temperature of 1100°C. The eco-cement showed non-hydraulic behavior and strength development required carbonation activation. As mentioned in above, sintering and carbonation activation has the potential to Immobilize the hazardous compounds present in MSWI residues, and the eco-cement comprehends both of these improvement processes. This chapter will study the effect of clinkering and carbonation on the environmental impact of the eco-cement, and this will ultimately benefit to commercially produce eco-cement concrete in large scale.

6.3 MATERIALS AND METHODOLOGY

6.3.1 MATERIALS

MSWI residues were collected form Emerald Energy from Waste (EFW) incinerator in Brampton Ontario. the raw feed (feed for the mix M2). There were three types of residues: bottom ash, boiler ash, and APC lime residues. Their chemical compositions were given in Chapter 3. They were dried and sieved to pass 10 mm size to remove large particles. The three ashes were then pulverized and used in a proportion of 28.80%, 28.80%, and 36.04 % respectively to make nodules of 10-20 mm size. Commercially available $Ca(OH)_2$ and SiO_2 were added by a mass ratio of 4.90 % and 1.47% respectively to the mixture proportion. The end eco-cement was made by about 94% incineration residues. This was batch M2 in Chapter 3 which was excellent for carbonation activation. These residues and virgin additives were then mixed in the proportion and the blend was pulverized. Nodules were produced using this pulverized blend and then calcined in a furnace. The sintering was carried out at 800°C for one hour to decalcify all the lime available, and then clinkering was carried out at 1100°C for one hour. After the clinkering, the clinkers were left to cool down slowly inside the furnace. Eco-cement was produced by pulverizing the clinkers to a cement size. Eco-cement paste was prepared with a w/c ratio of 0.10 using cylindrical compacts of 15 x 30 mm at a compressive load of 17 MPa. These compacts were then carbonated for two and twelve hours using 99.9 % pure CO_2 at a pressure of 1.5 bars for carbonation. Four samples were prepared separately to carry out each leaching test and bulk test. For leaching tests, as-received samples are used. They were (1) raw blend before nodulization and clinkering, (2) eco-cement after clinkering and pulverizing, (3) solid eco-cement compacts after two hours carbonation and (4) solid eco-cement compacts after twelve hours carbonation. For bulk tests, all samples including carbonated compacts were pulverized into powder form. They were (1) raw blend powder before clinkering, (2) eco-cement powder, (3) 2h-carbonated eco-cement powder and (4) 12h-carbonated eco-cement powder. The particle size for the powders was kept being lesser than 200 micrometers.

6.3.2 ENVIRONMENTAL TESTING

Environmental tests were carried in accordance with EPA SW-846, which are the test methods developed by environmental protection agency (EPA) for disposal and reuse of hazardous and non-hazardous solid waste. The environmental testing was performed for all the enlisted organic and non-organic contaminations that include heavy metals, dioxin and furans, volatile organic compounds (VOC) and polycyclic aromatic hydrocarbons (PAH). Two types of environmental testing were designed i.e. leaching testing and bulk testing. Leeching test is a very common and standardized type of test used to simulates the contact of the material with water. Leachates are extracted from the material by accelerated leaching techniques to simulate the water leaching process during the service life of material and then the environmental tests are performed on this leachate. Leaching can extract the free hazardous elements or the elements with weak bonds, strong bonds, and encapsulated material are difficult to extract. On the other hand, bulk tests were designed to find out the total amounts of elements present in the material. Materials are digested in appropriate strong solutions to measure the total quantities of elements. Bulk testing helped to understand the effect of clinkering and carbonation on the total amounts of the element. Bulk tests simulate the worst-case scenario if due to some unforeseen circumstances the strong bond or the encapsulation of hazardous elements devastated, and leaching vulnerability could be increased. Bulk testing results helped in forecasting the ultimate possible environmental risk of these hazardous elements.

6.3.2.1 LEACHING TESTS USING LEACHATES

These methods were adopted to measure the contaminations in the leachates of samples. The samples included raw blend powder, eco-cement powder, eco-cement compact after 2h carbonation and eco-cement compact after 12h carbonation. The tests of carbonated compacts were to determine the effectiveness of carbonation on immobilization of contaminants. For the dioxin and furans, the test was carried out in accordance with EPA 1613B with samples filtered if required. The solid portion was extracted by Soxhlet, and the liquid portion was liquid/liquid extracted with dichloromethane. The extracts were prepared using column chromatography, reduced in volume and analyzed by isotope-dilution Gas Chromatography Coupled with High-Resolution Mass Spectrometry (GC/HRMS). For heavy metals, inorganic and Semi-Volatile Organic contaminants were leached from waste samples strictly in accordance with US EPA Method 1311, "Toxicity Characteristic Leaching Procedure" (TCLP). Test results are reported in leachate concentration units (normally mg/L). PAH was measured as described by EPA SW-846 8270, samples were leached according to TCLP protocol and then the aqueous leachate was extracted, and the resulting extracts were analyzed on Gas Chromatography/Mass Selective Detector (GC/MSD). Depending on the analytical GC/MS column used benzo(j)fluoranthene may chromatographically co-elute with benzo(b)fluoranthene or benzo(k)fluoranthene. SW-846 8260 were used to measure the VOC, the sample of waste was leached in a zero-headspace extractor at 30–32 rpm for 1.8–2.0 hours with the appropriate leaching solution. After tumbling the leachate was analyzed directly by headspace technology, followed by GC/MS using internal standard quantitation.

6.3.2.2 BULK TEST FOR TOTAL CONTAMINANTS

The total quantities of contaminants present were also determined using a bulk test method to compare the amount available and the leachability of the contaminants. Samples included raw blend, eco-cement, eco-cement after 2h carbonation and eco-cement after 12h carbonation. All samples were pulverized to an OPC size and tested by extraction in different solutions according to the test methods. This is the worst scenario for leaching tests. EPA method 1613 B were used to determine the total amount of dioxin present in the sample. Samples were extracted by Soxhlet. The extracts were prepared using column chromatography, reduced in volume and analyzed by isotope-dilution Gas Chromatography Coupled with High-Resolution Mass Spectrometry (GC/HRMS). Metals in the samples were measured using EPA 6020A. This method used heated strong acid digestion with HNO3 and HCl and was intended to liberate metals that may be environmentally available. Silicate minerals were not soluble in acid. Dependent on the sample matrix, some metals may be only partially recovered, including Al, Ba, Be, Cr, Sr, Ti, Tl, V, W, and Zr. Volatile forms of sulfur (including sulfide) may not be captured, as they may be lost during sampling, storage, or digestion. The analysis is done by Collision/Reaction Cell ICPMS in accordance with the Protocol for Analytical Methods Used in the Assessment of Properties under Part XV.1 of the Environmental Protection Act (July 1, 2011). EPA 8270 testing method was followed to measure the total quantities of PAH in the samples. A representative sub-sample was fortified with deuterium-labeled surrogates and a mechanical shaking technique was used to extract the sample with a mixture of methanol and toluene. The extracts were concentrated and analyzed by GC/MS. VOCs were measured in accordance with EPA 8260, the samples were extracted in methanol and analyzed by headspace-GC/MS.

6.4 RESULTS AND DISCUSSIONS

6.4.1 TRACE METALS

Table 6.1 presents the trace metals based on TCLP results. Arsenic (As), Cadmium(Cd), Mercury(Hg), Selenium(Se), silver(Ag) and Uranium(U) remained unchanged before and after clinkering, and their quantities were lower than the detection limits. When the eco-cement was subjected to carbonation, the clinker phases transferred to new phases. After carbonation of eco-cement, leachability of As and Cd was increased by two- or twelve-hours carbonation. Carbonation curing reduces the pH, and these both metals mobilized at lower pH values. These findings were in agreement with the literature [37]. On the other hand, very high quantity of lead (Pb) was present in the raw MSWI residues, but it was fully immobilized during the clinkering and the quantity was reduced from 13.4 mg/l to less than 0.05 mg/l. The Pb remained Immobilized after the carbonation activation. Furthermore, the leaching of chromium (Cr) was increased in eco-cement after clinkering. It seemed that the Cr was released from the binding compounds during the clinkering. This leachable Cr was Immobilized into new reactive phases after the carbonation and was immobilized to the value of 5mg/l. These findings were slightly contradicting the past research, where carbonation of leachates increases the mobilization of Cr [36, 38]. In the case of eco-cement, the mobility of Cr could be hindered by the generated binding matrix. Carbonation activation helped the stabilization process by contributing in two ways. Firstly, carbonation activation densified the hardened matrix by the precipitation of micro-sized $CaCO_3$, the overall porosity and permeability were reduced, leading to a reduction in leaching physically. Secondly, the hazardous metals were impregnated into the reaction products as per the principal of cement stabilization of waste [39]. The Barium (Ba) content was reduced by both clinkering and carbonation. However, the Boron content was increased by clinkering and slightly decreased by carbonation.

The total quantities of metals present in the samples by bulk tests are given in Table 6.2. It was observed from the results that Cd, Cu, Pb, were more or less destroyed during the clinkering process, the total amount of these metals was reduced to one third or even lesser after the clinkering. Na and K were reduced to half and one-third reduction was observed in the Zn. The intensities of other metals were increased after the clinkering because there was a material loss during the clinkering process, that means the total amount of metals remained almost the same, but the total quantity of mix is reduced. The intensities of the metals were decreased after the two hours of carbonation and further decreased after twelve hours of carbonation. It was foreseeable, as the eco-cement amount remains the same, but some water and CO_2 was added i.e. the metals quantities remained same, but the overall quantity of material was increased, so densities of metal were reduced. In conclusion, the overall mobilization of heavy metals was Immobilized either by clinkering or by carbonation activation.

6.4.2 VOLATILE ORGANIC COMPOUNDS AND POLYCYCLIC AROMATIC HYDROCARBONS

The result of the TCLP results of VOC and PAH are presented in Table 6.3 and 6.4. It was observed from the results that the amount of VOC and PAH was less than the detection limits even in the raw blend, indicating a high-quality control of incineration at the incinerator facility. On the other hand, as presented in Table 6.5 and 6.6, the bulk testing result showed that the total amount of the majority of VOC and PAH were less than the detection limits. Only few VOC such as Acetone, Dichloromethane, Ethylbenzene, and o-Xyline were slightly above the detection limits, and these amounts were reduced during the clinkering process. Quantities of some PAH were also observed to be slightly higher than the detection limit and those were also fixed during clinkering. These PAH includes Anthracene, Benzo anthracene, Benzo fluoranthene, chrysene, Fluoranthene, Pyrene, Phenanthrene, Methylnaphthalene, and Naphthalene.

6.4.3 DIOXINS AND FURANS

Both tetra chlorinated dibenzo-p-dioxins (TCDD) and tetra chlorinated dibenzofurans (TCDF) were measured in TCLP leaching and bulk tests, and the results are presented in Table 6.7 and 6.8 respectively. There are 75 PCDD congeners based on the location and number of chlorine attached, seven are very toxic and most toxic being 2,3,7,8-TCDD. There are 135 isomers of chlorinated dibenzofuran, ten isomers have dioxin-like properties. The numbers in the name of dioxin and furans represent the number of chlorine atoms and their locations, for example; 2,3,7,8-TCDD represents tetra chlorinated dibenzo-p-dioxins with four chlorine atoms bonded at the locations of 2,3, 7 and 8 of parent compound dibenzo-p-dioxin. The numbering scheme remains identical in dioxins and furans, except the oxygen atoms in the parent compound. Dioxins have two atoms of oxygen bonded with chlorine atoms in the parent compound, but in furans, there is only one atom is bonded with chlorine atoms. The seven toxic dioxins and ten furans were measured in this research and the results are presented in Table 6.7 and Table 6.8. It was observed that the leaching of dioxin and furans were slightly increased after the clinkering, but these values are very close to the detection limits as shown in Table 6.7. The carbonation of eco-cement fixed this problem effectively and the amount of dioxin and furans were reduced to the detection limits. Researchers reported that elevated temperature of 800 °C or more, and an appropriate detention time could destroy the dioxin [17], this was proved in case of total dioxin testing. There were high values of dioxin and furans were observed in the raw meals, but after the clinkering, the dioxin and furans were almost destroyed and were very close to the detection limits of the instruments. Total quantities of TCDD and TCDF present in the samples are presented in Table 6.8. Clinkering process of eco-cement was a two-step process: firstly, the temperature of 800 °C was used for one hour to achieve decalcification of lime and then the temperature of 1100 °C for one hour to facilitate clinker phase formation. Due to these elevated temperatures and long retention times, the dioxin and furan compounds were destroyed. The value of TCDD was dropped to less than 0.59 pg/g after the clinkering from the total value of 41.6 pg/g present in the raw mixture. Similarly, the quantity of TCDF was dropped to 1.2 pg/g from 97.6 pg/g after clinkering. All the other congeners of PCDD and PCDF also showed identical results as of TCDD and TCDF. The TEQ for

6.5 CONCLUSIONS

In this research environmental impact assessment of eco-cement was conducted. EPA testing for the hazardous elements was carried out to observe the leaching behavior and the total amount of contaminants present in the samples. Furthermore, the effect of clinkering and carbonation was also evaluated. The conclusions are summarized below:

i. Two types of the testing scheme were designed; 1) leaching tests, 2) bulk tests. Leaching is the most commonly used test and these tests were carried out to simulate the extraction caused by water during the service life of the material. On the other hand, bulk tests were carried out to find the total quantities of elements present in the material.

ii. Clinkering process showed a mixed effect on the leachability of heavy metals, leachability of most of the metals was reduced after the clinkering such as Ba an Pb, but some metals such as Chromium and Boron showed an increase in the leaching properties. Carbonation activation Immobilized the Ba and Cr metals and reduced the values of metals in the leachates lesser than the regulatory limits. As and Cd was slightly mobilized due to the reduction of pH caused by carbonation, but all the metals were below the regulatory limits. On the other hand, the bulk testing showed that the clinkering process reduced the amounts of Cadmium, Copper, Sodium, Potassium and Lead to the one third or even lesser, these metals were probably vaporized during the clinkering process.

iii. Most of the PAH and VOC were found to be lesser than the detection limits of the instruments in both the leachates and bulk samples. Benzene and ethylbenzene were found slightly higher than the detection limits in the raw blend and were destroyed during the clinkering process.

iv. Dioxin and furans in the leachates were mostly found less than the detection limits, few types showed slightly high leachability after the clinkering process such as 2,3,7,8-TCDD and 1,2,3,4,6,7,8-HpCDD, but those were boned or encapsulated by carbonate products during the carbonation process. Furthermore, the long detention time at high temperature during the clinkering process of eco-cement destroyed all the types of dioxin and furans.

v. Clinkering process reduced the quantities of the hazardous materials present in the raw feed due to the elevated temperature treatment, at these high temperatures dioxins were destroyed and some metals were dissolved, and carbonation immobilized the elements either by reducing the pH or by encapsulating in the carbonation products. Combination of both clinkering and carbonation process either destroyed or immobilize all the hazardous elements and made the eco-cement environmentally safe.

Reference

1. Banar, M. and A. Özkan, *Characterization of the municipal solid waste in Eskisehir City, Turkey.* Environmental Engineering Science, 2008. **25**(8): p. 1213-1219.

2. Moy, P., N. Krishnan, P. Ulloa, S. Cohen, and P.W. Brandt-Rauf, *Options for management of municipal solid waste in New York City: A preliminary comparison of health risks and policy implications.* Journal of Environmental Management, 2008. **87**(1): p. 73-79.

3. Okada, T., Y. Tojo, N. Tanaka, and T. Matsuto, *Recovery of zinc and lead from fly ash from ash-melting and gasification-melting processes of MSW - Comparison and applicability of chemical leaching methods.* Waste Management, 2007. **27**(1): p. 69-80.

4. Lee, V.K.C., K.C.M. Kwok, W.H. Cheung, and G. McKay, *Operation of a municipal solid waste co-combustion pilot plant.* Asia-Pacific Journal of Chemical Engineering, 2007. **2**(6): p. 631-639.

5. Shi, H.s., K. Deng, F. Yuan, and K. Wu, *Preparation of the saving-energy sulphoaluminate cement using MSWI fly ash.* Journal of Hazardous Materials, 2009. **169**(1-3): p. 551-555.

6. Saikia, N., S. Kato, and T. Kojima, *Production of cement clinkers from municipal solid waste incineration (MSWI) fly ash.* Waste Management, 2007. **27**(9): p. 1178-1189.

7. Pan, J.R., C. Huang, J.J. Kuo, and S.H. Lin, *Recycling MSWI bottom and fly ash as raw materials for Portland cement.* Waste Management, 2008. **28**(7): p. 1113-1118.

8. Ginés, O., J.M. Chimenos, A. Vizcarro, J. Formosa, and J.R. Rosell, *Combined use of MSWI bottom ash and fly ash as aggregate in concrete formulation: Environmental and mechanical considerations.* Journal of Hazardous Materials, 2009. **169**(1-3): p. 643-650.

9. Aubert, J.E., B. Husson, and A. Vaquier, *Use of municipal solid waste incineration fly ash in concrete.* Cement and Concrete Research, 2004. **34**(6): p. 957-963.

10. Gupta, V.K., I. Ali, V.K. Saini, T. Van Gerven, B.D. Van Bruggen, and C. Vandecasteele, *Removal of dyes from wastewater using bottom ash.* Industrial and Engineering Chemistry Research, 2005. **44**(10): p. 3655-3664.

11. He, P.J., H. Zhang, C.G. Zhang, and D.J. Lee, *Characteristics of air pollution control residues of MSW incineration plant in Shanghai.* Journal of Hazardous Materials, 2004. **116**(3): p. 229-237.

12. Chang, C.Y., C.F. Wang, D.T. Mui, M.T. Cheng, and H.L. Chiang, *Characteristics of elements in waste ashes from a solid waste incinerator in Taiwan.* Journal of Hazardous Materials, 2009. **165**(1-3): p. 766-773.

13. Yang, J., B. Xiao, and A.R. Boccaccini, *Preparation of low melting temperature glass-ceramics from municipal waste incineration fly ash.* Fuel, 2009. **88**(7): p. 1275-1280.

14. Lee, V.K.C., W.H. Cheung, and G. McKay, *PCDD/PCDF reduction by the co-combustion process.* Chemosphere, 2008. **70**(4): p. 682-688.

15. Bie, R., S. Li, and H. Wang, *Characterization of PCDD/Fs and heavy metals from MSW incineration plant in Harbin.* Waste Management, 2007. **27**(12): p. 1860-1869.

16. Zhang, H.J., Y.W. Ni, X.P. Zhang, Q. Zhang, L. Zhao, N. Zhang, and J.P. Chen, *PCDD/F formation and its mass balance in a MSW incineration system.* Huanjing Kexue/Environmental Science, 2008. **29**(4): p. 1133-1137.

17. McKay, G., *Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: Review.* Chemical Engineering Journal, 2002. **86**(3): p. 343-368.

18. Quina, M.J., J.C. Bordado, and R.M. Quinta-Ferreira, *Treatment and use of air pollution control residues from MSW incineration: An overview.* Waste Management, 2008. **28**(11): p. 2097-2121.

19. Rui Lima , M.S., *Technical Note: An effective thermal technology for the detoxification of MSW fly ash.* Int. J. Environ. Technol. Manage, 2003. **Volume 3**(Issue 2): p. 212-218.

20. Izumikawa, C., *Metal recovery from fly ash generated from vitrification process for MSW ash.* Waste Management, 1996. **16**(5): p. 501-507.

21. Xiao, Y., M. Oorsprong, Y. Yang, and J.H.L. Voncken, *Vitrification of bottom ash from a municipal solid waste incinerator.* Waste Management, 2008. **28**(6): p. 1020-1026.

22. Jiang, J.C., M.; Zhang, Y.; Xu, X.; Luo, M. , *Sequestration of CO2 using municipal solid waste incinerator fly ash.* J. Tsinghua Uni, 2008. **48**: p. 5.

23. Xu, X., J.-g. Jiang, M.-z. Chen, M. Luo, Y. Zhang, and X.-j. Du, *[Investigation of the sequestration of CO2 and carbonation process for the stabilization of MSW fly ash]*. Huan jing ke xue= Huanjing kexue, 2007. **28**(7): p. 1644-1648.

24. Ferreira, C., A. Ribeiro, and L. Ottosen, *Possible applications for municipal solid waste fly ash.* Journal of Hazardous Materials, 2003. **96**(2-3): p. 201-216.

25. Yang, G.C.C. and T.-Y. Yang, *Synthesis of zeolites from municipal incinerator fly ash.* Journal of Hazardous Materials, 1998. **62**(1): p. 75-89.

26. Penilla, R.P., A.G. Bustos, and S.G. Elizalde, *Zeolite Synthesized by Alkaline Hydrothermal Treatment of Bottom Ash from Combustion of Municipal Solid Wastes.* Journal of the American Ceramic Society, 2004. **86**(9): p. 1527-1533.

27. Ho, Y.S. and G. McKay, *Comparative sorption kinetic studies of dye and aromatic compounds onto fly ash.* Journal of Environmental Science and Health, Part A, 1999. **34**(5): p. 1179-1204.

28. Ducom, G., D. Radu-Tirnoveanu, C. Pascual, B. Benadda, and P. Germain, *Biogas – Municipal solid waste incinerator bottom ash interactions: Sulphur compounds removal.* Journal of Hazardous Materials, 2009. **166**(2): p. 1102-1108.

29. Polowczyk, I., A. Bastrzyk, T. Koźlecki, W. Sawiński, P. Rudnicki, A. Sokołowski, and Z. Sadowski, *Use of fly ash agglomerates for removal of arsenic.* Environmental Geochemistry and Health, 2010. **32**(4): p. 361-366.

30. Sakai, S., S.E. Sawell, A.J. Chandler, T.T. Eighmy, D.S. Kosson, J. Vehlow, H.A. Van Der Sloot, J. Hartlén, and O. Hjelmar, *World trends in municipal solid waste management.* Waste Management, 1996. **16**(5-6): p. 341-350.

31. François, D. and K. Pierson, *Environmental assessment of a road site built with MSWI residue.* Science of The Total Environment, 2009. **407**(23): p. 5949-5960.

32. Mulder, E., *Pre-treatment of mswi fly ash for useful application.* Waste Management, 1996. **16**(1-3): p. 181-184.

33. Pera, J., L. Coutaz, J. Ambroise, and M. Chababbet, *Use of incinerator bottom ash in concrete.* Cement and Concrete Research, 1997. **27**(1): p. 1-5.

34. Cinquepalmi, M.A., T. Mangialardi, L. Panei, A.E. Paolini, and L. Piga, *Reuse of cement-solidified municipal incinerator fly ash in cement mortars: Physico-mechanical and leaching characteristics.* Journal of Hazardous Materials, 2008. **151**(2): p. 585-593.

35. Huang, W.-J. and S.-C. Chu, *A study on the cementlike properties of municipal waste incineration ashes.* Cement and Concrete Research, 2003. **33**(11): p. 1795-1799.

36. Ghouleh, Z. and Y. Shao, *Turning municipal solid waste incineration into a cleaner cement production.* Journal of Cleaner Production, 2018. **195**: p. 268-279.

37. Sanchez, F., C. Gervais, A.C. Garrabrants, R. Barna, and D.S. Kosson, *Leaching of inorganic contaminants from cement-based waste materials as a result of carbonation during intermittent wetting.* Waste Management, 2002. **22**(2): p. 249-260.

38. Wieser, T. and H. Weigand, *Stabilization of Heavy Metals in MSWI Bottom Ash by Enhanced Carbonation*. 2014.

39. Batchelor, B., *Overview of waste stabilization with cement.* Waste Management, 2006. **26**(7): p. 689-698.

Table 6.1: TCLP leaching of heavy metals results for the raw blend, eco-cement, and carbonated eco-cement.

Compounds/elements	Units	Raw blend	Eco-cement	2hr-c	12hr-c	D.L	R.L
Arsenic (As)	mg/L	<0.050	<0.050	0.187	0.165	0.05	5
Barium (Ba)	mg/L	1.19	0.7	0.52	0.59	0.5	100
Cadmium (Cd)	mg/L	<0.0050	<0.0050	0.0084	0.0232	0.005	1
Chromium (Cr)	mg/L	<0.050	14.1	4.85	4.95	0.05	5
Lead (Pb)	mg/L	13.4	<0.050	<0.050	<0.050	0.05	5
Mercury (Hg)	mg/L	<0.00010	<0.00010	<0.00010	<0.00010	0.0001	0.2
Selenium (Se)	mg/L	<0.025	<0.025	<0.025	<0.025	0.025	1
Silver (Ag)	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	0.005	5

2hr-c and 12hr-c: Eco-cement paste carbonation cured for two and twelve hours respectively

D.L: Detection Limit, R.L: Regulatory Limit

Table 6.2: Bulk amount of metals results for the raw blend, eco-cement, and carbonated eco-cement.

Metals	Unit	Raw	Clinker	2hr-c	12hr-c	D.L
Arsenic (As)	ug/g	47.9	71.7	70.1	51.7	0.1
Barium (Ba)	ug/g	318	338	252	200	0.5
Cadmium (Cd)	ug/g	209	8.13	8.03	6.54	0.02
Chromium (Cr)	ug/g	71.4	641	659	497	0.5
Lead (Pb)	ug/g	1870	210	79.2	86.2	10
Selenium (Se)	ug/g	2.37	0.36	0.45	0.41	0.2
Silver (Ag)	ug/g	12.2	5.14	3.45	3.06	0.1
Aluminum (Al)	ug/g	27200	37300	24500	18500	50
Antimony (Sb)	ug/g	395	776	804	611	0.1
Beryllium (Be)	ug/g	0.25	0.46	0.41	0.31	0.1
Bismuth (Bi)	ug/g	36.9	49	44.4	37.9	0.2
Boron (B)	ug/g	123	551	501	354	5
Calcium (Ca)	ug/g	250000	287000	288000	212000	50
Cobalt (Co)	ug/g	16.8	26.3	25.1	18.6	0.1
Copper (Cu)	ug/g	1800	621	509	408	10
Iron (Fe)	ug/g	14800	18100	17900	13900	50
Lithium (Li)	ug/g	23.8	33.7	32.8	22.2	2
Magnesium (Mg)	ug/g	19700	26300	25100	19600	20
Manganese (Mn)	ug/g	626	823	595	455	1
Molybdenum (Mo)	ug/g	11.1	17.1	16.9	14.6	0.1
Nickel (Ni)	ug/g	110	176	175	125	0.5
Phosphorus (P)	ug/g	4110	4900	4730	3490	50
Potassium (K)	ug/g	21600	10500	9820	7690	100
Sodium (Na)	ug/g	28800	18900	18000	13700	50
Strontium (Sr)	ug/g	289	341	346	264	0.5
Sulfur (S)	ug/g	39400	29700	42300	31400	1000
Thallium (Tl)	ug/g	0.197	<0.050	<0.050	<0.050	0.05
Tin (Sn)	ug/g	286	731	762	559	2
Titanium (Ti)	ug/g	1730	3350	3510	2600	1
Tungsten (W)	ug/g	1.77	3.84	3.7	2.9	0.5
Uranium (U)	ug/g	1.22	1.91	1.79	1.41	0.05
Vanadium (V)	ug/g	15.3	24.1	20.1	15.9	0.2
Zinc (Zn)	ug/g	9330	6730	6480	6180	40
Zirconium (Zr)	ug/g	19.6	6.7	8.3	5.9	1

2hr-c and 12hr-c= Eco-cement paste carbonation cured for two and twelve hours respectively D.L = Detection Limit

Table 6.3: TCLP leaching of Volatile organic compounds results for the raw blend, eco-cement, and carbonated eco-cement

Compounds/elements	Units	Raw blend	Eco-cement	2hr-c	12hr-c	D.L
1,1-Dichloroethylene	mg/L	<0.025	<0.025	<0.025	<0.025	0.025
1,2-Dichlorobenzene	mg/L	<0.025	<0.025	<0.025	<0.025	0.025
1,2-Dichloroethane	mg/L	<0.025	<0.025	<0.025	<0.025	0.025
1,4-Dichlorobenzene	mg/L	<0.025	<0.025	<0.025	<0.025	0.025
Benzene	mg/L	<0.025	<0.025	<0.025	<0.025	0.025
Carbon tetrachloride	mg/L	<0.025	<0.025	<0.025	<0.025	0.025
Chlorobenzene	mg/L	<0.025	<0.025	<0.025	<0.025	0.025
Chloroform	mg/L	<0.10	<0.10	<0.10	<0.10	0.1
Dichloromethane	mg/L	<0.50	<0.50	<0.50	<0.50	0.5
Methyl Ethyl Ketone	mg/L	<1.0	<1.0	<1.0	<1.0	1
Tetrachloroethylene	mg/L	<0.025	<0.025	<0.025	<0.025	0.025
Trichloroethylene	mg/L	<0.025	<0.025	<0.025	<0.025	0.025
Vinyl chloride	mg/L	<0.050	<0.050	<0.050	<0.050	0.05

2hr-c and 12hr-c: Eco-cement paste carbonation cured for two and twelve hours respectively D.L: Detection Limit

Table 6.4: TCLP leaching of polycyclic aromatic hydrocarbons compounds results for the raw blend, eco-cement, and carbonated eco-cement

Compounds/elements	Units	Raw blend	Eco-cement	2hr-c	12hr-c	D.L
Benzo(k)fluoranthene	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	0.005
Chrysene	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	0.005
Dibenzo(ah)anthracene	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	0.005
Fluoranthene	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	0.005
Fluorene	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	0.005
Indeno(1,2,3-cd)pyrene	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	0.005
Naphthalene	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	0.005
Phenanthrene	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	0.005
Pyrene	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	0.005
Quinoline	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	0.005

2hr-c and 12hr-c: Eco-cement paste carbonation cured for two and twelve hours respectively D.L: Detection Limit

Table 6.5: Bulk amount of volatile organic compounds results for the raw blend, eco-cement, and carbonated eco-cement

Compounds/elements	Units	Raw blend	Eco-cement	2hr-c	12hr-c	D.L
Acetone	ug/g	<1.7	<0.50	<0.50	<0.50	1.7
Benzene	ug/g	0.0716	<0.0068	<0.0068	<0.0068	0.0068
Bromodichloromethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Bromoform	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Bromomethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Carbon Disulfide	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Carbon tetrachloride	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Chlorobenzene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Dibromochloromethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Chloroethane	ug/g	<0.020	<0.020	<0.020	<0.020	0.02
Chloroform	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Chloromethane	ug/g	<0.020	<0.020	<0.020	<0.020	0.02
1,2-Dibromoethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Dibromomethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
1,2-Dichlorobenzene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
1,3-Dichlorobenzene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
1,4-Dichlorobenzene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Dichlorodifluoromethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
1,1-Dichloroethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
1,2-Dichloroethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
1,1-Dichloroethylene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
cis-1,2-Dichloroethylene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
trans-1,2Dichloroethylene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Dichloromethane	ug/g	<17.5	<0.050	<0.050	<0.050	18
1,2-Dichloropropane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
cis-1,3-Dichloropropene	ug/g	<0.030	<0.030	<0.030	<0.030	0.03
trans-1,3-Dichloropropene	ug/g	<0.030	<0.030	<0.030	<0.030	0.03
Ethylbenzene	ug/g	0.086	<0.018	<0.018	<0.018	0.018
n-Hexane	ug/g	<5.5	<0.050	<0.050	<0.050	5.5
2-Hexanone	ug/g	<0.50	<0.50	<0.50	<0.50	0.5
Methyl Ethyl Ketone	ug/g	<0.50	<0.50	<0.50	<0.50	0.5
Methyl Isobutyl Ketone	ug/g	<0.50	<0.50	<0.50	<0.50	0.5
MTBE	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Styrene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
1,1,1,2-Tetrachloroethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
1,1,2,2-Tetrachloroethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Tetrachloroethylene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Toluene	ug/g	<0.4	<0.080	<0.080	<0.080	0.4

1,1,1-Trichloroethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
1,1,2-Trichloroethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Trichloroethylene	ug/g	<0.010	<0.010	<0.010	<0.010	0.01
Trichlorofluoromethane	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Vinyl chloride	ug/g	<0.020	<0.020	<0.020	<0.020	0.02
o-Xylene	ug/g	<0.020	<0.020	<0.020	<0.020	0.02
m+p-Xylenes	ug/g	0.038	<0.030	<0.030	<0.030	0.03
Xylenes (Total)	ug/g	<0.050	<0.050	<0.050	<0.050	0.05

2hr-c and 12hr-c: Eco-cement paste carbonation cured for two and twelve hours respectively D.L: Detection Limit

Table 6.6: Bulk amount of polycyclic aromatic hydrocarbons compounds results for the raw blend, eco-cement, and carbonated eco-cement

Compounds/elements	Units	Raw blend	Eco-cement	2hr-c	12hr-c	D.L
Acenaphthene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Acenaphthylene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Anthracene	ug/g	0.055	<0.050	<0.050	<0.050	0.05
Benzo(a)anthracene	ug/g	0.089	<0.050	<0.050	<0.050	0.05
Benzo(a)pyrene	ug/g	0.054	<0.050	<0.050	<0.050	0.05
Benzo(b)fluoranthene	ug/g	0.09	<0.050	<0.050	<0.050	0.05
Benzo(g,h,i)perylene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Benzo(k)fluoranthene	ug/g	0.055	<0.050	<0.050	<0.050	0.05
Chrysene	ug/g	0.136	<0.050	<0.050	<0.050	0.05
Dibenzo(ah)anthracene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Fluoranthene	ug/g	0.341	<0.050	<0.050	<0.050	0.05
Fluorene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
Indeno(1,2,3-cd)pyrene	ug/g	<0.050	<0.050	<0.050	<0.050	0.05
1+2-Methylnaphthalenes	ug/g	0.156	<0.042	<0.042	<0.042	0.042
1-Methylnaphthalene	ug/g	0.075	<0.030	<0.030	<0.030	0.03
2-Methylnaphthalene	ug/g	0.082	<0.030	<0.030	<0.030	0.03
Naphthalene	ug/g	0.315	<0.013	<0.013	<0.013	0.013
Phenanthrene	ug/g	0.382	<0.046	<0.046	<0.046	0.046
Pyrene	ug/g	0.324	<0.050	<0.050	<0.050	0.05

2hr-c and 12hr-c: Eco-cement paste carbonation cured for two and twelve hours respectively D.L: Detection Limit

Table 6.7: TCLP leaching of dioxin and furans results for the raw blend, eco-cement, and carbonated eco-cement

Compounds/elements	Units	Raw blend	Eco-cement	2hr-c	12hr-c	D.L
2,3,7,8-TCDD	pg/L	<1.2	<1.4	<1.2	<1.2	1.2
1,2,3,7,8-PeCDD	pg/L	<1.2	<1.2	<1.2	<1.2	1.2
1,2,3,4,7,8-HxCDD	pg/L	<1.0	<1.0	<1.0	<1.0	1
1,2,3,6,7,8-HxCDD	pg/L	1.8	1.31	<0.98	<0.98	0.98
1,2,3,7,8,9-HxCDD	pg/L	1.2	<1	<1	<1	1
1,2,3,4,6,7,8-HpCDD	pg/L	2.8	3.4	<0.88	<0.88	0.88
OCDD	pg/L	5	5.3	<1.3	<1.3	1.3
Total-TCDD	pg/L	6.4	4.9	<1.2	<1.2	1.2
Total-PeCDD	pg/L	<1.2	<1.2	<1.2	<1.2	1.2
Total-HxCDD	pg/L	9.5	11.9	<1	<1	1
Total-HpCDD	pg/L	<0.88	<1.3	<0.88	<0.88	0.88
2,3,7,8-TCDF	pg/L	<1.4	<1.5	<1.4	<1.4	1.4
1,2,3,7,8-PeCDF	pg/L	<0.71	<0.90	<0.71	<0.71	0.71
2,3,4,7,8-PeCDF	pg/L	<0.60	<0.74	<0.60	<0.60	0.6
1,2,3,4,7,8-HxCDF	pg/L	1.75	1	<0.83	<0.83	0.83
1,2,3,6,7,8-HxCDF	pg/L	0.9	<0.86	<0.78	<0.78	0.78
1,2,3,7,8,9-HxCDF	pg/L	<1.1	1.2	<1.1	<1.1	1.1
2,3,4,6,7,8-HxCDF	pg/L	<0.79	<0.88	<0.79	<0.79	0.79
1,2,3,4,6,7,8-HpCDF	pg/L	1.45	<1.2	<0.46	<0.46	0.46
1,2,3,4,7,8,9-HpCDF	pg/L	<0.63	<1.8	<0.63	<0.63	0.63
OCDF	pg/L	1.9	<1.6	<1.6	<1.6	1.6
Total-TCDF	pg/L	<1.4	<1.4	<1.4	<1.4	1.4
Total-PeCDF	pg/L	<0.71	<0.90	<0.71	<0.71	0.71
Total-HxCDF	pg/L	1.8	<1.1	<1.1	<1.1	1.1
Total-HpCDF	pg/L	1.45	<1.8	<0.63	<0.63	0.63

2hr-c and 12hr-c: Eco-cement paste carbonation cured for two and twelve hours respectively D.L: Detection Limit

Table 6.8: Bulk amount of dioxin and furans results for the raw blend, eco-cement, and carbonated eco-cement

Compounds/elements	Units	Raw blend	Eco-cement	2hr-c	12hr-c	D.L
2,3,7,8-TCDD	pg/g	41.6	<0.69	<0.69	<0.69	0.69
1,2,3,7,8-PeCDD	pg/g	166	0.92	0.77	0.82	0.51
1,2,3,4,7,8-HxCDD	pg/g	136	<1.3	<1.3	<1.3	1.3
1,2,3,6,7,8-HxCDD	pg/g	177	0.89	1.2	<1.2	1.2
1,2,3,7,8,9-HxCDD	pg/g	192	<1.3	<1.3	<1.3	1.3
1,2,3,4,6,7,8-HpCDD	pg/g	1560	6.08	5.5	5.35	3.4
OCDD	pg/g	5230	17.7	14.1	14.9	1.8
Total-TCDD	pg/g	665	2.31	2.89	4.6	0.69
Total-PeCDD	pg/g	1250	9.88	0.77	2.17	0.51
`Total-HxCDD	pg/g	2030	7.69	5.78	5.26	1.3
Total-HpCDD	pg/g	2950	11.6	6.31	5.35	3.4
2,3,7,8-TCDF	pg/g	97.6	1.2	1.6	1.3	1.3
1,2,3,7,8-PeCDF	pg/g	212	0.69	1	0.9	0.69
2,3,4,7,8-PeCDF	pg/g	262	1.3	1.3	1.1	0.63
1,2,3,4,7,8-HxCDF	pg/g	411	<1.7	1.94	<1.7	1.7
1,2,3,6,7,8-HxCDF	pg/g	406	<1.6	<1.6	<1.6	1.6
1,2,3,7,8,9-HxCDF	pg/g	67.4	<1.9	<1.9	<1.9	1.9
2,3,4,6,7,8-HxCDF	pg/g	372	1.1	1.5	1.6	1.6
1,2,3,4,6,7,8-HpCDF	pg/g	2130	8.2	5.71	5.2	1.5
1,2,3,4,7,8,9-HpCDF	pg/g	131	<1.9	<1.9	<1.9	1.9
OCDF	pg/g	957	3.64	3.05	3.47	1.1
Total-TCDF	pg/g	3170	1.56	1.87	1.39	1.3
Total-PeCDF	pg/g	3770	5.33	5.18	6.12	0.69
Total-HxCDF	pg/g	3500	10.3	7.15	6.58	1.9
Total-HpCDF	pg/g	2740	9.81	6.51	6.33	1.9

2hr-c and 12hr-c: Eco-cement paste carbonation cured for two and twelve hours respectively D.L: Detection Limit

CHAPTER 7. CONCLUSIONS AND FUTURE WORK

7.1. CONCLUSIONS

This study has shown that the eco-cement can be made exclusively from municipal solid waste (MSWI) residues. Carbon dioxide was productively used to activate the strength gain of eco-cement. The eco-cement could be produced with more than 94% residues, had low energy requirements, and worked as a potential carbon sink. The following conclusions can be drawn.

1. A green low-energy ecological cement was made exclusively from municipal solid waste incineration residues, with the potential of sequestering CO_2 and conserving natural resources. This eco-cement will contribute towards environmental sustainability by utilizing the MSW incineration residues, reducing the landfill of waste material, reducing the carbon emission from cement production, and converting wastes into value-added products.
2. Eco-cement was produced at a different clinkering temperature ranging from 1000°C to 1300°C, but 1100°C was the optimum temperature in terms of conservation of energy, economy, and strength. Cement produced entirely from MSWI residues was more latent hydraulic and less sensitive to carbonation activation. While cement produced from 94% residues and 6% of additives of calcium oxide and silica oxide exhibited more reactivity to carbonation. Microstructural studies identified the chloroellestadite (CE) and belite as the major carbonation reactive phases. Chloroellestadite fixed the Chlorine and Sulphur in its composition and showed higher carbonation reactivity than the belite.

3. Eco-cement showed non-hydraulic behavior, and carbonation curing was used for strength development. Longer carbonation curing duration enhanced the compressive strength and was found to be a positive effect on the compressive strength of eco-cement. The 12-hours carbonation strength was 50% higher than the 2-hours carbonation strength of eco-cement.
4. Carbonation curing of CE and belite phases resulted in the formation of $CaCO_3$, gypsum, an increase in the amorphous phase. The amorphous phase is most likely the amorphous calcium silicate hydrocarbonate. TGA and FTIR confirmed the presence of calcium carbonate, gypsum, and calcium silicate hydrocarbonate.
5. SEM/EDS showed the packing density and reactivity of twelve hours carbonation curing is much better than that of two hours carbonation curing. The presence of amorphous calcium silicate hydrocarbonate phase was also observed by SEM/EDS. TEM analysis helped to confirm the presence amorphous phase (calcium silicate hydrocarbonate) and $CaCO_3$ were also identified in TEM micrographs, which revealed that the carbonation derived a matrix of eco-cement is mainly composed of amorphous calcium silicate hydrocarbonate.
6. To understand the strength development mechanism of eco-cement, synthesized CE and belite were produced and carbonated for different durations. It was observed during the studies, the mix of synthesized CE and belite showed higher average compressive strength than the average compressive strength of individual synthesized components. It was also observed that the CE was a non-hydraulic material and belite showed negligible hydraulic properties at the early age of hydration. Carbonation curing for twelve hours had improved the microstructure as compared to two hours carbonated samples by decreasing physical

porosity, growing the microstructure in all free spaces, producing denser microstructure and converting the maximum amount of CE into new phases.

7. TGA confirmed the presence of calcium carbonate, gypsum, and C-S-H in the carbonated synthesized CE and the in a mix of CE and belite. SEM clearly showed the transformation of CE into another fibrillar spindle-shaped microstructure. EDS suggested that this phase likely to be amorphous calcium silicate hydrocarbonate, a C-S-H like a phase.
8. The microstructure of eco-cement was analogous to the microstructure of synthesized mixed CE and belite, but the size of the reaction product was smaller than the size of synthesized mix reaction products. Presence of impurities/ unreacted phases in eco-cement could be the reason for this reduction in size and the amount of reaction products.
9. It can be concluded that the superior binding strength of carbonated eco-cement is due to the combination of mechanical and chemical actions. Chemical action includes the formation of calcium carbonate, calcium silicate hydrocarbonate, and gypsum. Mechanical action consists of high packing density and friction bond of nanoparticles of fibrillar shaped microstructure produced by carbonation of CE, leading to a dense microstructure after prolonged carbonation curing. Cement paste strength of the eco-cement after 2-hours of CO_2 curing was comparable to the 28-days hydrated paste of the OPC. Furthermore, the practical use of the binder in concrete was demonstrated by using granite aggregate, ecological cement concrete showed almost equal strength to the OPC concrete; Moreover, this strength was also higher than the concrete brick strength requirements of CSA-A165.
10. Two types of the environmental testing scheme were designed; 1) leaching tests, 2) bulk tests. Leaching is the most commonly used test and these tests were carried out to simulate

the extraction caused by water during the service life of the material. On the other hand, bulk tests were carried out to find the total quantities of elements present in the material.

11. Clinkering process showed a mixed effect on the leachability of heavy metals, leachability of most of the metals was reduced after the clinkering such as Ba an Pb, but some metals such as Cr and Ba showed an increase in the leaching properties. Carbonation activation Immobilized the Ba and Cr metals and reduced the values of metals in the leachates lesser than the regulatory limits. The metals As and Cd was slightly mobilized due to the reduction of pH caused by carbonation, but all the metals were below the regulatory limits. On the other hand, the bulk testing showed that the clinkering process reduced the amounts of Cd, Cu, Na, K and Pb to the one third or even lesser, these metals were probably vaporized during the clinkering process.
12. Most of the PAH and VOC were found to be lesser than the detection limits of the instruments in both the leachates and bulk samples. Benzene and ethylbenzene were found slightly higher than the detection limits in the raw blend and were destroyed during the clinkering process.
13. Dioxin and furans in the leachates were mostly found less than the detection limits, few types showed slightly high leachability after the clinkering process such as 2,3,7,8-TCDD and 1,2,3,4,6,7,8-HpCDD, but those were bonded or encapsulated by carbonate products during the carbonation process. Furthermore, the long retention time at high temperature during the clinkering process of eco-cement destroyed all the types of dioxin and furans.
14. Clinkering process reduced the quantities of the hazardous materials present in the raw feed due to the elevated temperature treatment, at this high-temperature dioxins were destroyed and some metals were vaporized, and carbonation immobilized the elements either by a

reduction in the pH or by encapsulating in the carbonation products. Combination of both clinkering and carbonation process either destroyed or immobilize all the hazardous elements and made the eco-cement environmentally safe.

15. Finally, the goal is to convert the incineration facility into a cement production plant by utilizing the waste residues generated as a raw meal for cement production, the heat energy produced during burning of waste material for clinkering and emitted CO_2 will be utilized to cure/ activate the binder. Moreover, the consistency in the performance of the new binder produced using MSWI ashes from different seasons over the year emphasized the practicality of this study.

7.2. FUTURE WORK

- The detailed experimental investigation can also be made for the eco-cement produced entirely from MSWI residues.
- To achieve better early carbonation strength and increased subsequent hydration strength, blend of both early strength gaining eco-cement (produced using 6 % of pure calcium oxide and silica oxide) and high subsequent hydration strength gaining eco-cement (entirely derived from MSWI residues) shall be studied.
- TGA coupled with MS can be used to study the exact elements of decomposition of eco-cement after heating beyond 800 °C.
- Eco-cement can be used to produce eco-concrete, the durability of eco-concrete shall be studied.