

**Synthesis of Value-Added Zeolites and Tobermorite from Waste Glass
Cullet using Conventional and Microwave-Assisted Hydrothermal
Treatments**

by

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A Thesis submitted to the Faculty of Graduate Studies of

The University of Manitoba

in partial fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

Department of Civil Engineering

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Winnipeg

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Abstract

The ever-increasing volume of the waste glass cullet (WGC) is becoming a global environmental concern due to the majority of it being discarded in landfills. In US, only, 10 million tons of WGC were generated in 2013 with roughly 26% recycling for the post-consumer applications. As a result, the estimated WGC landfilling in North America is above 60% while landfilling could not potentially be an environmentally friendly alternative. Hence, reusing the massive amounts of WGC towards the synthesis of value-added products like zeolites and tobermorite could be a greener option to overcome this challenge.

In terms of zeolitization of WGC, a great attention was paid in this research to utilizing novel sources of energy such as microwave (MW) radiation to accelerate the induction period and shorten the crystallization time. Results showed that 10min of radiation was sufficient for the synthesis of zeolite at 150°C with almost similar crystallinity than that of the one which was treated for 24h using a conventional heating oven. However, specific radiation conditions should be taken in to account especially if the synthesis is conducted under autogenous pressure. Experimental data obtained in this work verified the adverse effect of high temperature/ pressure environment on the nucleation and crystallinity of zeolites. This overshoot in pressure and temperature was found to be relevant to the ionic conductivity of the reaction mixture, which could affect the MW interaction with the gel components. Landfill leachate was also found to be a promising alternative aqueous media for the zeolitization of WGC and produced zeolites with higher crystallinity compared to the deionized water. This approach could pave the way for the facile reusing of a hazardous waste stream such as leachate towards the production of value-added zeolites, due to high cost and complexity of the processes are currently used for its treatment.

Synthesis of Al substituted 11Å tobermorite using WGC as the precursor was also studied in the current work. The key parameters to prepare a well crystalline pure 11Å tobermorite were as follows: 180°C reaction temperature, 5h of reaction time, 0.5M of activator concentration, and Ca/Si ratio of 0.83. Various analytical techniques confirmed that Al substitution occurred preferentially for the bridging and branching sites within the dreierketten silica chains resulting in an enhanced polymerization degree of the silica chains. This improvement within the microstructure by the impact of the Al substitution could broaden the application of 11Å tobermorite particularly in the environmental and construction sectors.

Overall, the results obtained in this study showed that MW radiation could significantly reduce the zeolite crystallization time due to fast and homogenous nucleation. However, increasing the power of radiation in the reaction vessel without efficient monitoring the temperature and pressure overshoot could result in the synthesis of poorly crystalline phases. The introduction of a fusion pretreatment prior to the crystallization was found to be significantly influential on the improvement of the WG zeolites properties including the crystallinity and cation exchange capacity compared to the direct hydrothermal synthesis. The reusage of the landfill leachate towards the synthesis of zeolites also was a promising alternative for the aqueous phase and provided zeolites with comparable properties as deionized water. WGC was found as a cheap suitable alternative for the synthesis of pure well crystalline 11Å tobermorite. The Al content within the WGC matrix successfully substituted within the layered microstructure of the synthesized 11Å tobermorite. This would increase the polymerization degree of the silica chains in the dreierketten structure, which could potentially improve the mechanical properties, ion exchange properties, and stability of the prepared 11Å tobermorite.

Declaration

I, Alireza Majdinasab, declare that the thesis, which I hereby submit for the degree Doctor of Philosophy at the University of Manitoba, is my original own work and has not previously been submitted for any other degrees at this or any other tertiary institution.

Alireza Majdinasab

July 2020

*To my beloved father,
Mansoor Majdinasab*

Co-Authorship Statement

Chapter 3

Article Title: -
Cost-effective zeolite synthesis from waste glass cullet using energy efficient microwave radiation
Authors:
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Article status:
Published, Materials Chemistry and Physics
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Majdinasab, A. R., Manna, P. K., Wroczynskyj, Y., van Lierop, J., Cicek, N., Tranmer, G. K., & Yuan, Q. (2019). Cost-effective zeolite synthesis from waste glass cullet using energy efficient microwave radiation. <i>Materials Chemistry and Physics</i> , 221, 272-287.

Chapter 4

Article Title:
Microwave synthesis of zeolites from waste glass cullet using indirect fusion and direct hydrothermal methods: A comparative study
Authors:
Alireza Majdinasab, Qiuyan Yuan
Article status:
Published, Ceramics International
A.R. Majdinasab did the experimental design, performed all the lab work related to the synthesis and characterization of the samples, did data interpretation, and wrote the paper. Prof. Q. Yuan supervised the project and reviewed the paper.

Majdinasab, A. R., & Yuan, Q. (2019). Microwave synthesis of zeolites from waste glass cullet using indirect fusion and direct hydrothermal methods: A comparative study. *Ceramics International*, 45(2), 2400-2410.

Chapter 5

Article Title:

Microwave synthesis of zeolites from waste glass cullet using landfill leachate as a novel alternative solvent

Authors:

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Article status:

Published, Materials Chemistry and Physics

A.R. Majdinasab did the experimental design, performed all the lab work related to the synthesis and characterization of the samples, did data interpretation, and wrote the paper. Prof. Q. Yuan supervised the project and reviewed the paper.

Majdinasab, A., & Yuan, Q. (2019). Microwave synthesis of zeolites from waste glass cullet using landfill leachate as a novel alternative solvent. *Materials Chemistry and Physics*, 223, 613-622.

Chapter 6

Article Title:

Synthesis of Al-substituted 11Å tobermorite using waste glass cullet: A study on the microstructure

Authors:

Alireza Majdinasab, Qiuyan Yuan

Article status:

Published, Materials Chemistry and Physics

A.R. Majdinasab did the experimental design, performed all the lab work related to the synthesis and characterization of the samples, did data interpretation, and wrote the paper. Prof. Q. Yuan supervised the project and reviewed the paper.

Majdinasab, A., & Yuan, Q. (2020). Synthesis of Al-substituted 11Å tobermorite using waste glass cullet: A study on the microstructure. *Materials Chemistry and Physics*, 123069.

Acknowledgements

Completing my PhD at the University of Manitoba is one of the most wonderful yet challenging experiences that I have ever had. I am grateful for having the opportunity to do my PhD research in such a well-equipped institution. So, I thank the University of Manitoba, Manitoba Institute for Materials (MIM), the Nanomagnetism Research Group, Manitoba Liquor and Lotteries, Department of Civil Engineering, Department of Geology and Rady Faculty of Health Sciences College of Pharmacy for their excellent and friendly environment that has provided for us. I'm truly honoured of being part of such a great and exceptional research team.

To my supervisor, Prof. Qiuyan Yuan, I am blessed and thankful for having you by my side through my degree. Apart from being the best supervisor and role model, you were also like a caring mother since the first day I arrived. You always encouraged me to do my best and gave me the best advice and help when I needed. I could not have imagined having a better advisor and mentor for my PhD study.

To my committee member, Prof. Hartmut Hollaender, I would like to say a big thank you for all the help, support and guidance. I have learnt so much from you not only in the field of science but also some lessons for life. I cannot find the words to thank you enough for what you did for me.

I would like to express my sincere gratitude to my other committee member, Prof. Johan van Lierop, for the continuous support of my PhD study and related research, for his patience, motivation, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis.

I would like to give a big thank you to Manitoba Liquor and Lotteries, and again Department of Civil Engineering for all the financial support. Without their trust in my abilities, completing this degree would have not been possible. I am also grateful to the following university staff: Palash

Manna, Victor Wei, Mark Cooper, Abdul Khan, and Ravinder Sidhu for their unfailing support and assistance during my PhD research.

To my parents and specially my father, thank you for your support and prayers. You have provided me through moral and emotional support in my life. Your words always encouraged me to continue and eventually finish this challenging path.

I thank my lab mates and friends, Amir Shirzadi, Abbas Jafari, Saeideh Mirzaiee, Cornelia Andrea Badila, Kadir Yanach, Jinger Labayan, Parvin Berenjkari, Pouria Jabbari, and Fernanda de Matos Ferraz for the stimulating discussions, for the sleepless nights we were working together before deadlines, and for all the fun we have had in the last four years.

And finally, last but by no means least, also to everyone in the Environmental Engineering Group. It was great sharing laboratory with all of you during last four years. Being away from my motherland would have been very difficult without the caring friends that I met and I will never forget their kindness towards me. Thanks for all your encouragement!

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Chapter 1. General introduction

1.1. Background

Waste glass cullet (WGC) can be re-used in glasswork, construction aggregate, or as sand replacement in water purification. In Manitoba, most glass bottles are crushed and used as aggregate for road-base. Eventhough various recycling programs are applied, Canada annually generates 850000 tones of WGC with still half portion being dumped in landfills (Majdinasab and Yuan, 2019). Recycle Alberta estimates that one tonne of natural resources can be saved by recycling one tonne of glass (Alberta Recycling Market Profile (ARMP), 1997). A significant increase of recycling rates, though important to sustainable development, seems unlikely due to the economic and technical constraints. The issues such as the presence of inorganic, organic, and mixed color contamination, could be the main causes of economic and technical challanges. This could result in adverse environmental impacts as the volume of the WGC disposal within landfill sites is increasing globally. It is roughly estimated that the total WGC disposal in landfills globally is around 200 million tons annually, while a very limited amount recycled (Jiang et al., 2019). According to a report by US Environmental Protection Agency (USEPA), 11 million tons of WGC was generated in US only in 2011, with just 28% recycling rate (USEPA, 2015). In addition, the relatively low value of the final products such as road aggregates and glasswork could be a prohibitive factor as it may not offset the high cost for glass recycling. This makes the glass recycling business economically unattractive. One solution to this problem is to produce higher value-added products such as zeolites and tobermorite to make the process more economically attractive. Since zeolites possess unique physicochemical properties, they are widely used as adsorbents, ion exchangers, molecular sieves, and catalysts. Hence, they could contribute remarkably to industries including gas/water purification, petrochemistry, pollution controlling, and radioactive waste management (Bukhari et al., 2015). Tobermorite also due to its unique

properties has shown a wide application as insulation in building materials, ion exchanger for the radioactive waste management, and adsorbent (Guo et al., 2017).

1.2. Environmental remediation of zeolites

Zeolites have gained significant research focus to expand their broadened applications to protect the environment. This could be mainly attributed to their three main abilities to act as efficient adsorbents, ion exchangers, and catalysts. Therefore, zeolites have a widespread applications including mining, agriculture, solvent separations, paper industry, petrochemical processes, and water purification and softening ((Bukhari et al., 2015). However, the main remediation applications of zeolites are regarding water and wastewater treatment. Various sources of industrially processed wastewater sources, such as those originated from rinsing, leaching, or mining, are potentially contaminated with soluble and/or particulate organic matters as well as toxic heavy metals (Bukhari et al., 2015). Several research teams could be interested in the green zeolitic fields of applications ranging from separation and purification technologies to environmental remediation and protection, specifically wastewater cleaning.

Synthetic zeolites could potentially have wider applications rather than natural zeolitic minerals due to the main advantages the former could have over the latter. These advantages including the superior thermal and chemical stability as well as engineering the structure to produce zeolites with a broaden range of pore sizes and chemical properties (Visa, 2016). The zeolitic materials are famous due to their unique properties that could uptake and keep toxic heavy metals within their framework. Heavy metals removal has become a major environmental hazard according to the adverse impacts they may have on water and soil due to their toxicity and escalating discharge (Chen et al., 2018). The accumulation of remarkable amounts of ammonium within the discharged effluents and receiving waters is also of a paramount concern to the environment since

eutrophication could result in the algal contamination of the surface waters (Yao et al., 2019). Hence, using zeolitic materials for the removal of organic and inorganic contaminants from aqueous environments has gained a significant consideration.

1.3. Environmental remediation of tobermorite

Calcium silicate hydrates (CSHs), especially tobermorite, have been considered as efficient industrial fire retarding and heat insulant building materials (Guo et al., 2017). They are also the main binder components within ordinary Portland cement (OPC) monitoring the concrete characteristics including durability and mechanical properties (Guo et al., 2017). Apart from construction sector, CSHs are gaining remarkable attention for their heavy metal removal potential (Kuwahara et al., 2013). There are several advantages, which make CSHs an appropriate option for the removal of heavy metals from industrial wastewater effluents. These profits include high ion exchange capacity, low toxicity, and availability of low-cost precursors for their synthesis (Ma et al., 2018).

So far, pioneering studies have focused on producing efficient CSHs to uptake heavy metals from contaminated water (Ma et al., 2018; You et al., 2016). The most well-known procedure is the synthesis via hydration of OPC or other sources of binders. The main drawback of this method is the impurity of the resultant gel as it makes the CSH separation complicated. This may result in the heavy metal removal process unfeasible at large scales (Richardson, 2008). The second method involves the utilization of chemical reagents as calcium and silicon sources coupled with advanced ultrasound dispersion to produce uniform CSHs with desirable properties (Zhao et al., 2014). However, the wide application of the CSHs derived by chemicals for the large-scale removal of heavy metals could be remarkably restricted. This could be attributed to the high synthesis costs as well as low easy access to the precursors.

In order to mitigate the drawbacks mentioned above, the third alternative is to utilize low-cost readily available wastes to produce CSHs with desirable properties. Several studies have reported the utilization of calcium and silica enriched wastes including blast furnace slag, fly ash, and oyster shells as low-cost starting materials to produce CSHs of high quality (You et al., 2016; Kuwahara et al., 2013). This work investigates the synthesis of tobermorite (as a commonly used CSH) using WGC as a promising precursor.

1.4. Motivation and Objective

Canada recycles less than one-half of the estimated 850,000 tons container glass in the market place on an annual basis ((Majdinasab and Yuan, 2019). It is important to create a market-place for value-added utilization of recycled glass to drive recycling rates and reduce disposal in landfills. Applications in utilizing recycled crushed glass as an aggregate material in concrete and asphalt, reflective beads for road paints and roadbed aggregates have been reported. Current glass separation and screening activities that are employed in material diversion facilities across Canada leave a glass stream that can include contaminants including ceramics, trace metals, hard plastics (i.e. bottle caps), and other organics (i.e. some paper, corks, etc). The proposed research could provide a new market for this relatively impure recycled WGC, if crushed and pulverized glass can be utilized as a feedstock for zeolites and tobermorite synthesis.

The synthesis of zeolites and tobermorite using WGC is a hydrothermal reaction conducted in hyper-alkaline solutions. Since the efforts made in pioneering studies regarding the conversion of various aluminosilicate-enriched wastes to value-added zeolites and tobermorite mainly implemented conventional heating (CH) methods, lots of work has been done to investigate the synthesis of the mentioned products utilizing ultrasound (UTS) and microwave (MW) energies. The present work considered the utilization of the novel MW radiation for the zeolitization of the

WGC and provided a thorough comparison with the materials synthesized using CH method. The other main objective of this study is the conversion of the WGC into a value-added tobermorite using CH method.

This thesis mainly focused on the application of novel sources of energy such as MW radiation for the WGC conversion into zeolites. A single-mode lab-scaled MW apparatus produced by CEM Company was used to conduct the MW synthesis experiments. Multi-mode MW, like kitchen MW units, could generate set of waves with various phase shifts, while a single-mode MW directs electromagnetic waves in a way to produce a standing wave of a specific phase shift.

The procedures for the production of tobermorite and zeolitic materials could be costly; hence, their wide application in environmental and construction sectors are limited. Low-cost precursors such as WGC, fly ash, and kaolinite could potentially mitigate the synthesis cost restrictions. Among the mentioned materials, utilization of WGC to produce tobermorite and zeolites is studied in the current work with the evaluation of their potential remediation applications. It is worth mentioning that majority of the applications may operate under specific conditions quite different from the actual lab-scaled ones. Therefore, the current work could shed light on the knowledge and prediction of the WGC utilization at large-scale commercial tobermorite and zeolites manufacturing.

1.5. Thesis outline and structure

The organization of this thesis is an integrated sandwich format in accordance to the template specified by the Faculty of the Graduate Studies at the University of Manitoba. In the first part of Chapter 2, a comprehensive literature review will be provided over the recent achievements regarding the zeolite synthesis using waste materials, especially coal fly ash, with the application of new MW and UTS energies. Various zeolitization methods with their differences will also be

discussed as well as the impact of several synthesis parameters on the efficiency of zeolite crystallization. The second part of Chapter 2 exhibits a literature survey on the relation between the structure and composition of the CSHs as well as their synthesis using different calcium and silica enriched wastes.

Chapter 3 will discuss a facile procedure to reuse WG cullet, and produce value-added zeolites using a rapid MW synthesis technique. The detailed objectives of this part are as follows: i) to investigate the formation of zeolitic materials from WG cullet via MW radiation technique and to compare the generated phases with materials synthesized through a CH method under the same synthesis conditions; and ii) to provide a comprehensive comparison between the performance of two different MW synthesis modes; i.e. constant temperature (MWCT) and constant power (MWCP); in terms of the nucleation and crystallization efficiency.

Chapter 4 describes synthesis of zeolites from WGC using indirect fusion synthesis (IFS) method by MW hydrothermal treatment in order to increase the silica dissolution rate, WGC conversion rate, and crystallinity of the synthesized zeolites. The primary objective of this part is to provide a comparison between direct hydrothermal synthesis (DHS) and IFS conversion methods utilizing MW radiation in terms of gel growth mechanism, nucleation, and crystallinity of the samples. Secondly, a comprehensive comparison between the performance of two different MW synthesis modes, i.e., MWCT and MWCP modes using both DHS and IFS methods was provided. The effect of MW cooling air jet on the efficient monitoring of the temperature and pressure within the vessel in MWCP mode and crystal growth of the products was also studied. Chapter 5 investigates the effect of using landfill leachate instead of DI water on types and quantities of zeolites synthesized from WG cullet by MW radiation. The effect of the MW interaction with landfill cations on the crystallinity of the synthesized zeolites was also studied.

Chapter 6 explores the reuse of WGC and convert it to a more value added product i.e. Al-substituted 11 A° tobermorite. In order to consider the effect of Al substitution on the microstructure and properties of 11 A° tobermorite, Al-free and Al-substituted 11 A° tobermorite samples will be synthesized and characterized. The way Al substitution may affect the tobermorite properties such as microstructure, thermal properties, functional groups, and composition will be investigated.

Chapter 7 will briefly discuss the main engineering significance and the way this work could potentially contribute to the industry. Chapter 8 summarizes the overall conclusions extracted out of this thesis, according to the obtained results and conducted experiments. This chapter also presents recommendations for the future research prospect.

Chapter 2. Literature review

Abstract

The worldwide increase in the volume of the waste by-products such as waste glass cullet and coal fly ash (CFA) requires urgent research efforts. Therefore, conversion of these wastes into the value-added products such as zeolites and tobermorites could be the best alternative to overcome this challenge. This chapter, in the first part, will review the recent developments in the zeolitization of CFA using hydrothermal treatment synthesis with a main focus on the application of novel energy sources such as microwave radiation as compared with conventional heating technique. Various applications of zeolites due to their unique framework structures and thermochemical stability has also been discussed. Due to the accelerated aluminosilicates dissolution and nucleation, the induction period and consequently reaction time could be remarkably declined. In the second part, a thorough explanation over the composition/structural relationships among different polymorphs of tobermorite family will be provided. The tobermorite-like minerals are quite meta stable and their synthesis could be monitored via multiple parameters including type of the precursor, reaction time, reaction temperature, and Ca/Si ratio. Hence, obtaining pure well-crystalline phase within this system could be very complicated. The hydrothermal synthesis of tobermorite at different conditions according to the experimental work conducted in the literature as well as its thermodynamic equilibrium with xonotlite has also been extensively discussed. Lack of clear information regarding the optimum conditions at which the layered tobermorite structure could be hydrothermally stable has aroused a huge controversy over understanding the transformation mechanism. Therefore, further research should be conducted to shed light on finding the optimal synthesis conditions.

2.1. Introduction

Waste glass (WG) landfilling has raised an imperative environmental issue due to the shortage of land in populated areas, increased consumption of natural resources as well as a concentrated focus on mitigating the effect of greenhouse gases on the construction sector. Ancient Egyptians and Syrians were the first ones to produce glass around 3500 BCE. Early reports revealed that glass had found its place as an essential merchandise in Europe by the late 1400s and beginning of 1500s (Macfarlane and Martin, 2002). WG production rate has remarkably accelerated ever since then. It is believed that all types of glasses have a restrained lifecycle, although glass is chemically neutral (Majdinasab and Yuan, 2019; Zheng, 2016). This convinced researchers to explore new procedures to reduce the WG dumping rate in landfills. Preliminary recycled glass applications were restricted to beads, bowls, and jars; however, the level of glass utilization has enormously evolved to include solar panels, lighting applications, shelves, windows, appliances, and fiber optic cables due to the emersion of new technologies in glass manufacturing industry (Bansal and Doremus, 2013). Implementation of glass in various applications has risen because of the inclusion of cullet possessing different features such as desirable levels of flakiness index, fineness modulus, shape index, specific gravity, and bulk density. The most well known types of glass include borosilicate glass, lead glass, soda-lime-silica glass, crystal glass, and electronic glass.

The production of glass has been thoroughly investigated (Klein et al., 2015). The preliminary stages in production of glass commodities include extracting, conveying and treating the raw materials to obtain glass of the desired composition (Freestone et al., 2003). Then, the cullet feedstock is conveyed to a manufacturing plant where the batches are co-melted with the charged recycled cullet (Abbassi and Khoshmanesh, 2008). It is estimated that one metric ton of recycled glass is virtually made up of 64 Kg of feldspar, 560 Kg of sand, and 176 Kg of limestone (Andreola et al., 2007). The main reason of failure in recycling a large fraction of WG in the glass

manufacturing plants is attributed to the variable chemical composition of glass. Glass is not a biodegradable material. Therefore, when a portion of non-recyclable glass is dumped in landfills, it can take up to a million years for a glass bottle to degrade. This disposal strategy is occupying precious space that should be dedicated to the biodegradable wastes.

The WG generation rate from the municipal solid waste in 2013 was roughly 10.37 million tons in the U.S., out of which beverage and food bottles accounted for the largest fraction (U.S. E.P.A., 2015). Only 27% of the generated WG were recycled for secondary applications, while the remaining (7.59 million tons) were dumped in landfills. On the other hand, European countries generated 1.5 million tons of WG because of demolition and renovation as well as 15.9 million tons because of packing glass wastes (Obe et al., 2018; da Cruz, 2014). In 2007, 130 million tons of glass were produced worldwide due to the subsequent evolution of the glass manufacturing industry (Rahim et al., 2014; Topcu and Canbaz, 2004). Out of the substantial amount of recycled cullet, only a tiny portion could be re-charged to the glass manufacturing furnaces due to the stringent quality restrictions faced by most glass manufacturers. Conventional glass recycling methods involve the collection and sorting of the WG sources based on their colors. The WG source cannot be sorted by mixed color as it is crushed and mixed with the other sources, which make it technically and economically implausible to be remanufactured due to the presence of contaminants (Day et al., 1970). Several challenges during the remanufacturing of the mixed-color WG sources include the distinct melting temperature of each glass type as well as incompatibility in terms of the chemical composition. It is reported that 5 g of glass with the mixed-color problem, which makes it non-recyclable, is sufficient to contaminate a ton of recyclable glass (Afshinnia and Rangaraju, 2015). The WG reutilization is a process that greatly benefits the environment by replacing the depleting natural resources by WGC. It also reduces the energy demand of glass manufacturing process since the temperature required for melting the recycled glass is typically

lower than that is necessary for melting the raw materials used for glass production (Afshinnia and Rangaraju, 2016). The European countries recycled up to 73% of the glass packing waste in 2015 and the highest recoveries of WG were obtained in Germany, Belgium, Sweden, and Luxemburg (Figure 2-1) (Europe, 2016).

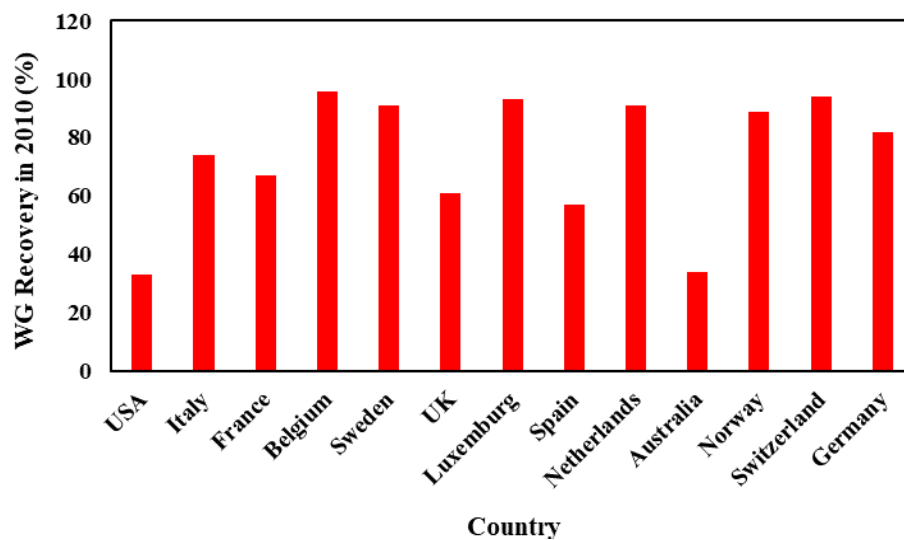


Figure 2-1. WG recovery of some countries in 2010 (Europe, 2016)

In 2004, United Nations estimated that 181.4 million tons of solid waste was generated while glass accounted for 12.7 million tons (Topcu and Canbaz, 2004). Considering the fact that construction sector generated roughly 92.5 million tons of asphalt concretes and 4.6 million tons of cement in 2013 and 2015, respectively, the efforts for finding substitute materials to minimize the utilization of natural resources have gained higher attention (Du and Tan, 2017). With the main goal of reducing the burden of WG disposal from landfills as well as minimizing the huge demand of natural resources in construction sector, researchers have been strongly focused on developing secondary application of WG in road and construction industries (Mohajerani et al., 2017; Ukwatta et al., 2016). Cullet has been investigated for its use as aggregates in the construction sector ranging from concrete and cementitious materials to roadway and asphalt construction. In addition, WG can also be utilized in manufacturing of ceramic-based products.

2.2 Waste glass (WG) cullet properties

2.2.1. Physical properties

Due to the remarkable morphology of WGC, it is defined by physical features such as flakiness index, fineness modulus, specific gravity, bulk density, and shape index (Terro, 2006). Table 1 presents the values of these major WGC physical features. The ratio of weight to volume of WG cullet is known as bulk density. Shape index, which is defined as a fraction of the overall dry weight of the examined grains, is the cullet mass when the length/thickness proportion exceeds three. The modulus of fineness is expressed as the summation of the overall fraction of the aggregate cullet remaining on every specific succession of sieves, while the cumulative amount is obtained based on 100% of the fraction (Terro, 2006). The fraction, by weight, of the cullet with the minimum diameter smaller than 0.6 times of the median diameter is defined as the flakiness index (Stanworth, 1950). The range of the flakiness index, fineness modulus, and specific gravity (Table 2-1) depends on the variable composition and processing conditions of the WG cullet.

Table 2-1. Several physical features of WG cullet

Property	Value	Ref.
Flakiness Index	84.4-94.7	Disfani et al. (2011)
Fineness modulus	0.43-3.29 4.25	Lee et al. (2013)
Specific gravity	2.4-2.8 2.52 (Amber), 2.5 (Green)	Park and Lee (2004)
Bulk density	1360 Kg. m ⁻³	de Castro and de Brito (2013)
Shape Index (%)	4.25	Lee et al. (2013)

2.2.2. Chemical properties

Table 2-2. Chemical composition of some well-known commercially used glasses (Park and Lee, 2004)

Glass type and application	SiO ₂	Al ₂ O ₃	NaO ₂	B ₂ O ₃	K ₂ O	CaO	MgO	PbO	BaO	Others
<i>Lead glass</i>										
Optical dense flint	32		1		2			65		
Electronic parts	56	2	4		9			29		
Neon tubing	63	1	8		6			22		
Color TV funnel	54	2	4		9			23		
<i>Borosilicate glass</i>										
Tungsten sealing	74	1	4	15						
Pharmaceutical	72	6	7	11	1					
Chemical equipment	81	2	4	13						
<i>Soda-lime-silica glass</i>										
Tempered ovenware	75	1.5	14			9.5				
Lightbulbs	73	1	17			5	4			
Sheet	71-73	0.5-1.5	12-15			8-10	1.5-3.5			
Float	73-74		13.5-15		0.2	8.7-8.9	3.6-3.8			
Containers	66-75	0.7-7	12-16		0.1-3	6-12	0.1-5			
<i>Aluminosilicate glass</i>										
Resistor substrates	57	16		4		10	7		6	
Fiberglass	64.5	24.5	0.5				10.5			
Combustion tubes	62	17	1	5		8	7			
<i>Barium glass</i>										
Optical dense barium crown	36	4		10				41		9% ZnO
Color TV panel	65	2	7	2	9	2	2		2	10% SrO

SiO₂ - Silicon dioxide; Al₂O₃- Aluminum dioxide; NaO₂- Sodium oxide; B₂O₃- Bore oxide; K₂O- Potassium oxide;
 CaO- Calcium oxide; MgO- Magnesium oxide; PbO- Lead oxide; BaO- Barium oxide

Glass is typically manufactured with distinct colors that comprise different chemical compositions. The variable chemical features of the mixed color WG cullet is potentially the major reason impeding the high glass recovery rate. Based on their composition, glasses could be used in different applications including electronics, TV panels, laboratory glassware, optics, fiberglass, and containers. The most well known types of glass include borosilicate glass, lead glass, soda-lime-silica glass, crystal glass, and electronic glass. The chemical compositions for some of the most well known marketable glasses are represented in Table 2-2.

2.3. Recovery methods of post-consumer cullet

Approximately, 89% of the post-consumer cullet originates from food and beverage bottles of different colors including green, amber, and flint (Teixeira et al., 2004). Upon collection, the cullet is transported to the material recovery facility (MRF) where the collected cullet is processed and subsequently delivered to the local markets. Initially, the cullet is sorted and separated from other recyclables by means of either mechanical magnetic separation or manual handpicking (Teixeira et al., 2004). In the second stage, the cleaned cullet is transported to a pulverizer for increasing the particles' fineness. Optical sorting instrument may also be available at some recycling facilities, based on the post-consumer market demand. This advanced technology greatly improves the separation of glass from non-glass particles as well as the sorting of cullet based on different colors.

2.4. Challenges restricting cullet recycling for post-consumer market

One of the major concerns restricting cullet recycling for post-consumer market is the cullet contamination. The main contaminants include mixed color glass, light bulbs, metals, ceramics, and cookware. Organics such as food scraps, paper, and plastics could also be a source of potential contamination. Truck handling compaction and the breakage of cullet occurring during this period often leads to inaccurate separation of glass from contaminants, which restricts the post-consumer

market demand for cullet supply. The problem is also highlighted by severe regulations imposed by some consumers such as the glass container or fiberglass manufacturers. These consumers can solely use cullet of the same color and composition. Therefore, the WG cullet should be initially sorted in terms of the color and be free of any other contaminant. The presence of contaminants also damages the desirable glass melting conditions and causes harmful glass tinge to the glass (Teixeira et al., 2004). Hence, Synthesis of zeolites and tobermorite could be a promising alternative to reduce the volume of landfilled WG.

Zeolites are crystalline microporous structures with tetrahedral of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ connected at the corners of a three dimensional framework. At elevated temperatures, the precipitation of zeolites out of an aluminosilicate enriched hyper-alkaline solution occurs. Coal fly ash (CFA) is a source of silicates and aluminates that has extensively used for the zeolite synthesis. After a pioneering study conducted by Holler and Wirsching (1985), several patents as well as numerous publications have reported the CFA potentials for zeolitization. This conversion mainly occurs using a hydrothermal reaction within a highly alkaline solution media. The main stages of reaction involves the solubility of the aluminosilicates, followed by nucleation and ultimately crystallization.

Since zeolite synthesis is an energy-consuming process, elevated temperatures are required for the crystal to grow and the energy is provided by the conventional means of heating. So far, novel sources of energy including microwave (MW) and ultrasound have been reported as an alternative for the conventional heating methods (Bukhari et al., 2015). Several studies have confirmed that the synthesis time could be significantly reduced using these novel energies (Rohani et al., 2010). With this strategy not only value added zeolites with multiple industrial and environmental

applications are synthesized, but also a large volume of waste could be reused instead of being dumped off in landfills.

2.5. Microwave (MW) properties

On the electromagnetic spectrum, MW is located between radio and infrared waves with the frequency of operation of 2.45 and 0.915 GHz. Due to the more availability of magnetrons commercially as well as the greatest absorption capacity of water at this frequency, the application of 2.45 GHz is more prevailing (Li and Yang, 2008). There are several advantages of MW radiation over conventional heating (CH) mainly due to the remarkable different energy transfer mechanism. The MW interaction with the components within the solution including the ions and Dielectric molecules is the main mechanism of this energy transfer. In this mechanism, the electromagnetic field sets dipolar molecules into oscillation and the molecules will then follow the oscillations. The collisions between the molecules and ions would restrain their thermal motion. As a result, heat is generated due to the energy dissipation by the inter-molecular collision. This leads to a more uniform heat generation compared to the CH.

Moreover, some studies have also reported non-thermal MW impacts apart from the thermal properties. In the case of the liquid under pressure, the MW radiation could promote the temperature to beyond the normal boiling point. This phenomenon is caused due to the suppression of the bubble nuclei by the high ambient pressure, which is called “super heating” effect (Perreux and Loupy, 2001).

2.5.1. MW heating versus conventional heating (CH)

Conventionally, organic/inorganic synthesis reactions involve the heating the reaction media using a conventional source of energy including hot ovens or oil baths. The main drawback of this method is prolonged synthesis times as the surface of the vessel should be heated firstly, and the

hot surface will then transfer the heat to the reaction media. In contrast, efficient internal heating occurs in the case of MW radiation mainly due to the oscillation of the dipolar molecules and ions as a result of the applied electromagnetic field. Due to the transparency of the reaction vessel, the MW could penetrate through the solution heating the mixture on a molecular basis. Hence, an inverted temperature gradient as well as low wall effects would occur in MW radiation rather than CH (Perreux and Loupy, 2001). The difference between heat transfer mechanism of the CH and MW radiation techniques is illustrated in Figure 2-2.

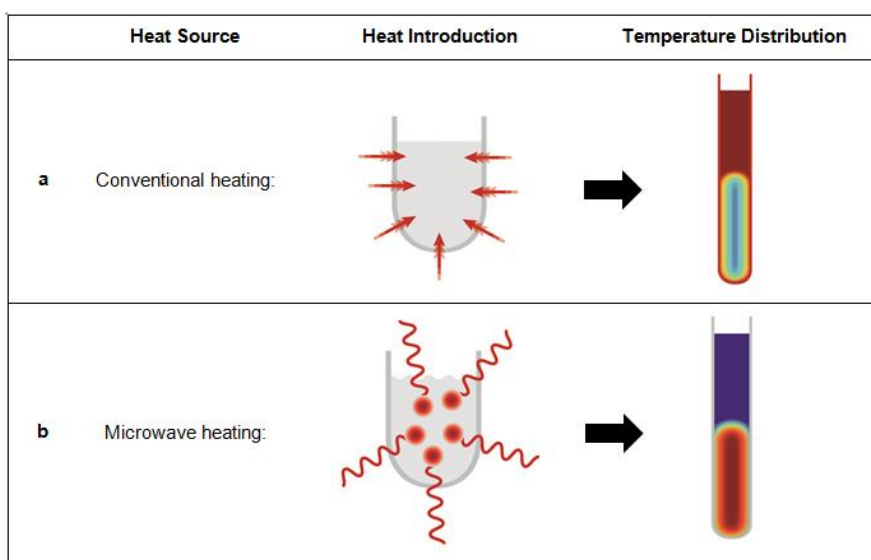


Figure 2-2. Illustration of the different temperature profiles within the reaction mixture for a) CH and b) MW radiation (Kappe et al., 2012)

In addition, the electromagnetic energy conversion and rate of heat generation could be remarkably fast and efficacious, could not be reproduced by CH. Another advantage is that due to the rapid temperature rise up to the target, by-products formation is considerably restricted leading to higher productivity of the synthesis (Kappe et al., 2012). Due to these unique properties, MW synthesis of zeolites using waste precursors as well as pure chemicals have been extensively investigated in the literature, which is the main discussion topic of this chapter.

2.6. Zeolite structure and characteristics

Zeolites are microporous crystalline structures of alkali and alkali earth. Apart from being naturally available, various waste materials as well as chemicals could be utilized to synthesize them. The zeolitic structural framework is mainly described by the porous cavities, which are occupied by the metal cations and water molecules. The three dimensional tetrahedral of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ linked at corners extensively construct the zeolite frameworks. The connection of $[\text{SiO}_4]^{4-}$ tetrahedral potentially produces a neutral framework, while the $[\text{AlO}_4]^{5-}$ substitution with $[\text{SiO}_4]^{4-}$ tetrahedral introduces net negative charge on the surface of the framework (isomorphous substitution).

The residential cations within the cavities are responsible for electrically counterbalancing the negative charge introduced in the zeolitic framework due to the isomorphous substitution. Hence, higher portion of $[\text{AlO}_4]^{5-}$ within the framework would provide a zeolite with higher cation exchange capacity. The cations within the porous cavities are kept by means of weak electrostatic interactions, which could reversibly undergo ion exchange for other cations. The overall chemical formula of a zeolitic unit cell could be described as follows:



In this formula, M indicates the cations capable of being exchanged mostly of alkali or alkali earth groups. However, other organic, metallic, or non-metallic cations may also be present in the cavities to keep the framework neutral in terms of electric charge. The valence of the cation is represented by n. Since two adjacent tetrahedral could not be occupied by $[\text{AlO}_4]^{5-}$, the X value ranges between at least 2 or higher. The number of water molecules per unit cell is represented by Z (Ali Zaidi and Rohani, 2005).

The chemical properties of the zeolitic materials are remarkably impacted by the relative location and amount of $[\text{AlO}_4]^{5-}$ tetrahedral within the framework. The Si/Al ratio could be significantly variable; for instance, the infinity Si/Al ratio expresses a pure silicate structure. The catalytic properties as well as ion exchange capacity of zeolites remarkably rely on the net negative charge provided by the Al tetrahedral. The content of $[\text{AlO}_4]^{5-}$ tetrahedral within the framework also determines the degree of hydrophilicity, hydrophobicity, and the adsorption of polar/no-polar compounds (Ali Zaidi and Rohani, 2005). The mentioned properties should be monitored as they have considerable impact on the zeolite application. Tetrahedral of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ are considered as the primary building units (PBUs) of the zeolitic structures. The connection of these PBUs would build up specific arrangements, which are characteristic of a zeolite framework and considered as secondary building units (SBUs). The Zeolite Framework Types Atlas has published a list of 218 novel zeolite structure types. In this Atlas, the International Zeolite Association Committee has represented each structure type by a 3-letter code (Baerlocher et al., 2007). Table 2-3 summarizes the properties for some of the common zeolites structure types. Figure 2-3 also illustrates the structures of these common zeolite frameworks.

2.7. Zeolitized Coal Fly Ash (CFA) various applications

Three main functional properties of synthetic and natural zeolites including ion exchange, catalytic, and adsorption properties could remarkably affect their applications. Hence, zeolites could be widely used in sectors such as water/wastewater treatment, waste management, petrochemical industry, agriculture, and gas purification (Tanaka et al., 2008). Due to the presence of impurities, zeolites synthesized by wastes such as CFA may not have as broaden application as those produced by pure chemicals. To overcome this challenge, significant research effort has been made to evaluate the various applications of zeolitized CFA. In one study in order to adsorb SO_2 out of a stack gas containing 2% SO_2 (by volume), zeolites Na-P1, X, and Y were produced using

CFA by Srinivasan and Grutzeck (1999). Under a pretreatment at 150°C for 7 days, the most efficient CFA specimen was synthesized with the

Table 2-3. The unit cell information, combined building units (CBUs), and types of zeolites for some of the common frameworks

Framework	Unit cell data		Zeolites	CBU
	Geometry	Lattice constants		
CHA	Trigonal	a= 13.7Å, c= 14.8Å	SAPO-47, Chabazite, SAPO-34	D6r, Cha
ANA	Cubic	a= 13.6Å	Analcite, AIPO-24	
EDI	Tetragonal	a= 6.9Å, c= 6.4Å	Edingtonite, Linde-F, K-F, Zeolite N	Nat
MER	Tetragonal	a= 14.0Å, c= 10.0Å	Merlinoite, Linde-W, Zeolite W, K-M	Dcc, D8r, Pau
SOD	Cubic	a= 9.0Å	Hydroxysodalite, SOD, AIPO-20	Sod
LTA	Cubic	a= 11.9Å	Zeolite-A, SAPO-42	D4r, Sod, Lta
FAU	Cubic	a= 24.3Å	Faujasite, Na-Y, Na-X, ZSM-20	D6r, Sod
GIS	Tetragonal	a= 9.8Å, c= 10.2Å	Na-P, Na-P1, Gismondine, SAPO-43	Gis

removal capacity of 6-7 mg of SO₂ for each g of the specimen. In another study, zeolitized CFA was produced to separate CO₂ from a flue gas by Majchrzak-Kuceba and Nowak (2005). They reported that the Na-A zeolite synthesized using CFA adsorbed roughly 52 mg of CO₂ per each g of the zeolite. The impregnation of the zeolites Na-P1 and Na-A with silver was also reported by

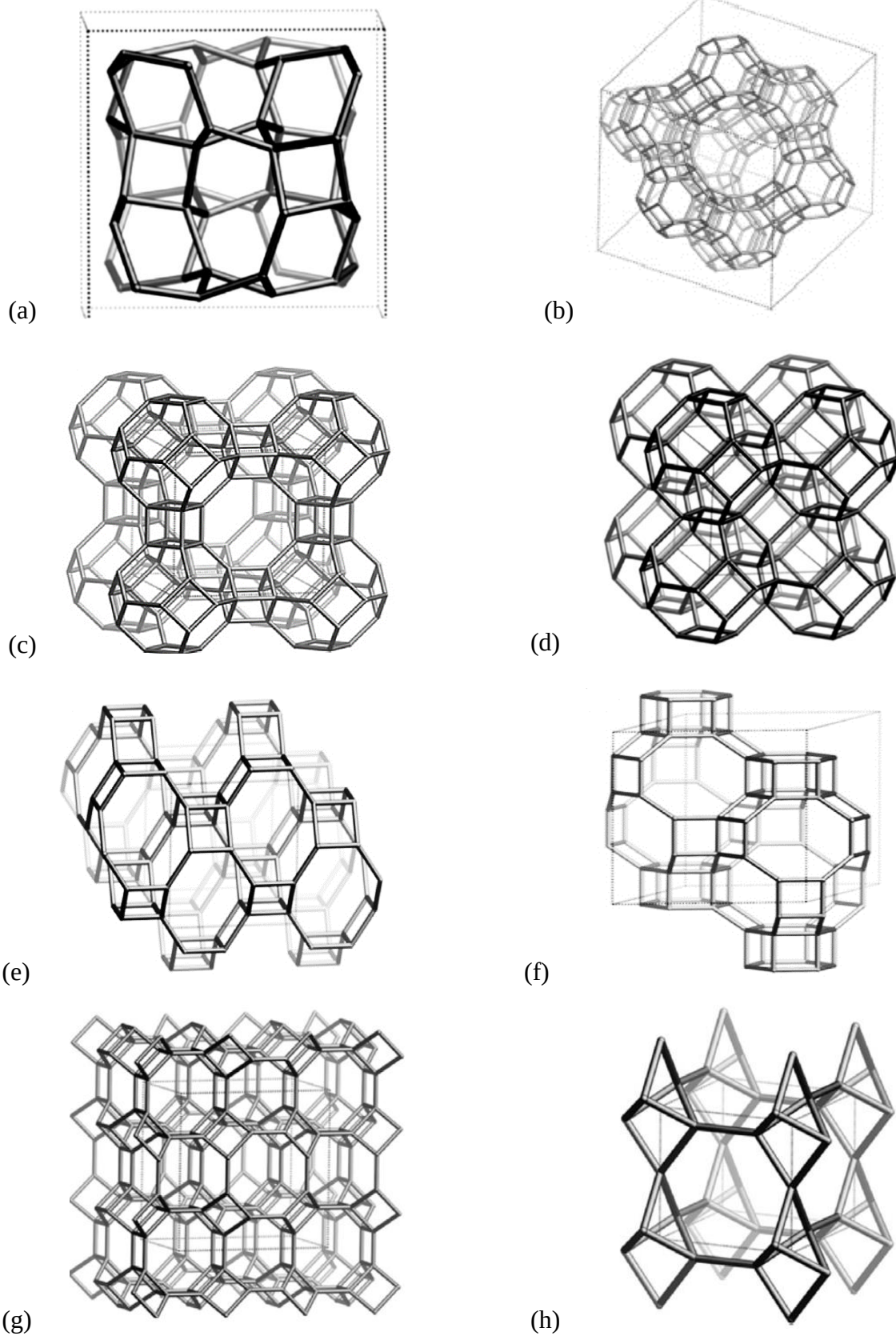


Figure 2-3. Some of the zeolitic common structure types (a) ANA, (b) FAU, (c) LTA, (d) SOD, (e) GIS, (f) CHA, (g) MER, (h) EDI (Bukhari et al., 2015)

Wdowin et al. (2014) and used for the Hg removal. The CEC of the zeolitized CFA is by far the most important property affecting their prevailing applications. This unique feature could be efficient in the removal of the heavy metals from the contaminated waters. Hence, synthesis of the zeolitized CFA with remarkable CEC has gained high attention in the literature. In one study, Berggaut and Singer (1996) reported the CEC between 5.78 and 6.12 meq/g by the replacement of Na^+ with NH_4^+ . In another study, Woolard et al. (2000) at 90°C for 21h treated 0.1Kg CFA in 1000 mL of the NaOH solution with the concentration of 1 to 8M. They reported that the lead removal rate at pH of 5.0 was 1.00 meq/g and maximum CEC obtained was 3 meq/g. The zeolitized CFA has also been widely investigated for the heavy metals removal including Mo, Pb, Ar, Cu, Cd, Co, Ni, Zn, V, Tl, U, and Sb from polluted water sources (Ghasemi et al., 2018; Taamneh and Sharadqah, 2017).

The zeolitized CFA was also used for the separation of water from an aqueous solution ethanol. For this aim, Klamrassamee et al. (2010) synthesized zeolitized CFA, which provided water removal capacity reproducible by the molecular sieves commercially available on the market. Functionalization of zeolites to clean up oil spills has also been investigated by Sakthivel et al. (2013). They synthesized a zeolitized CFA and then embedded octyl, octadecyl, and propyl alkyl functional groups on the surface to make the zeolite hydrophobic enough to adsorb spills of oil. In this case, they produced an environmentally friendly zeolite with the spill removal capacity of the 1.2 g for each g of the modified zeolitic adsorbent. The broaden applications of the zeolitized CFA have also extensively discussed in a reviews by Ahmaruzzaman (2010) and Collins et al. (2020). There are huge research efforts made in the literature to expand the applications of the zeolites synthesized by wastes such as CFA. Gas purification, water treatment, environmental remediation, and catalysis are the major but not all of these applications. Having discussed the main profits of the zeolites synthesized by wastes including CFA compared to the chemically synthesized zeolites,

production of these value-added materials could be a huge motivation to utilize these ever-increasing wastes.

2.8. Conversion steps of aluminosilicate wastes to zeolites

As mentioned earlier, the aluminosilicate wastes are mainly composed of minerals of silicates and aluminates. However, exhibiting a long-range structural order is the major difference between such wastes and zeolitic materials. While these wastes mainly contain amorphous aluminosilicate phases, zeolites have well-defined crystalline structures. Considering the compositional similarities, these wastes, especially CFA, have widely been utilized as starting precursors for the zeolite synthesis (Gollakota et al., 2019). The whole process occurs under hydrothermal conditions within a hyper alkaline solution in which the main components of the waste (i.e. silicoaluminates) are converted to crystals of zeolites. The conversion firstly starts by the dissolution of the silicates and aluminates; and then condensation of the soluble aluminosilicates to form a three-dimensional network of amorphous hydrated aluminosilicates. The poly-condensation step is followed by nucleation, and ultimately crystal growth. In the case of CFA, all the conversion steps to zeolite structures are schematically illustrated in Figure 2-4.

The first step of the zeolitization, which is the dissolution of the aluminosilicates in the solution, strongly affects the rate of conversion, as it could be the slowest step of the reaction (Gollakota et al., 2019). Although specific zeolite frameworks could be synthesized by adjusting the ratios of the silicates to aluminates, the Al and Si could have variable concentrations at different locations. The mechanism for the zeolitization of wastes such as CFA could be potentially different compared to the zeolites synthesized by chemical reagents. This could be mainly attributed to the lower solubility of the aluminosilicates of the waste matrix as well as the availability of some cationic metals that may inhibit or contribute to the crystallization of some phases (Gollakota et al., 2019). For instance, Rayalu et al. (2001) reported that it would be vital to select the target

zeolite structure to be synthesized from a specific CFA as the presence of some cationic elements could suppress a particular zeolite while suppressing another.

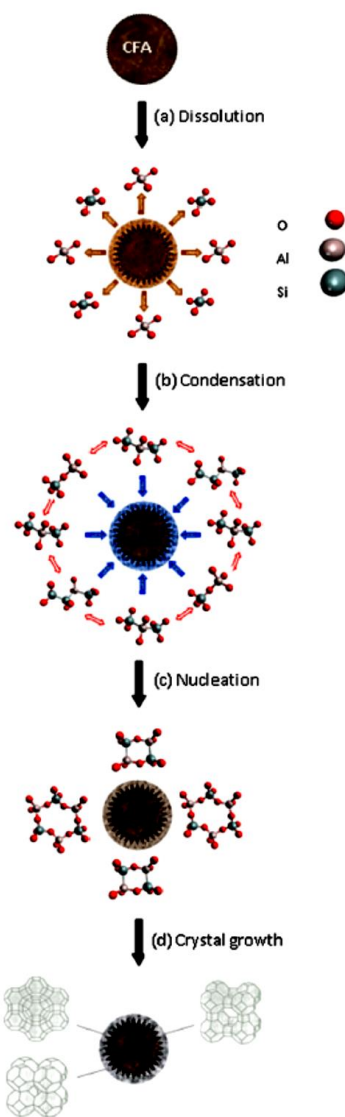


Figure 2-4. Schematic illustration of the various steps of CFA zeolitization including a) Aluminosilicates dissolution from CFA matrix, b) Poly condensation of the aluminosilicate polymeric chains, c) Zeolite nucleation, and d) Zeolite crystal growth (Bukhari et al., 2015)

The CFA residues were remarkably detected within the synthesized zeolites even after prolonged reaction times of 1 to 3 days (Tauanov et al., 2018). The lower CEC of the zeolitized CFA compared to the pure zeolites has also attributed to the presence of the large CFA residues

(Tauanov et al., 2018). The availability of the crystalline phases within the matrix of the aluminosilicate waste could also retard the zeolite nucleation, as these phases are resilient against alkali diffusion. This could be the case for mullite conversion in CFA, while the glassy aluminosilicates within the matrix would simply dissolve in the solution (Rayalu et al., 2001).

2.9. Direct hydrothermal synthesis (DHS)

2.9.1. DHS using CH methods

The DHS method starts with the dissolution of the waste such as CFA in a hyper alkaline media to transfer sufficient aluminates and silicates into the solution as well as to provide the heat required for the following steps including the poly-condensation, nucleation, and ultimately crystal growth of zeolites. To produce the target zeolite, the Si/Al could be adjusted by adding the aluminates and silicates sources. Hence, according to the synthesis conditions including seeding, Si/Al ratio, pressure, temperature, reaction time, aging time, pH, and type and concentration of the template, various zeolites such as zeolite Na-A, Na-X, Chabazite, Hydroxysodalite, Na-P1, and analcime (Bukhari et al., 2015).

The DHS method was used at three temperatures of 180°C, 200°C, and 250°C by Wirsching (1975) to synthesize zeolites analcite, philipsite, and chabazite using volcanic glass. He confirmed that the waste materials could be considered as promising starting precursors for the zeolite synthesis. In another study, zeolite Na-P1 was synthesized by Hollman et al. (1999) from CFA using DHS method by dissolving 0.5 Kg of CFA within 1250 mL of the 2M of NaOH solution. In the next step, the mixture was heated at 90°C for 96h for the hydrothermal reaction to proceed. They approved the formation of the zeolite nuclei on the CFA external surface and reported that as soon as these nuclei reach a certain amount and size the crystal growth occurs. In another part of the experiment the same mixture was first prepared and then underwent a hydrothermal incubation for

6h at 90°C through a two-step process. The adjustment of the Si/Al ratio between 0.8 and 2 was conducted after the filtration and drying of the incubated solution. Next, the filtrate with the adjusted ratio was heated for 48h at 90°C followed by the filtration of the incubated mixture and drying of the separated solids. Many studies have focused on the zeolitization of the CFA using CH methods which some of them are summarized in Table 2-4.

Table 2-4. Summary of the studies investigated zeolitized CFA synthesis using CH methods

Studies	Type of zeolite	Synthesis conditions			NaOH/CFA	Crystallization conditions
		t (h)	T(°C)	NaOH (M)		
Murayama et al. (2002)	Na-P1	3-24	120	0.5-4	0.08-0.64	
Moreno et al. (2002)	Na-X, Na-A	39	80-90	2.0	0.24	Used wastewater
Ma et al. (1998)	Na-P1	48	25	2.8-5.0	0.28-0.5	144h and 100°C
Park et al. (2000)	Na-P1	12	103	3.0	0.5	
Inada et al. (2005)	SOD, Na-P1	24	100	3.5, 2.0	1.12, 0.64	
Hui and Chao (2006)	Na-A	2	100	2.0	0.8	1.5h and 90°C
Derkowski et al. (2006)	Na-P1	24	105	1.0	0.8	Using NaCl solution of 3M
Juan et al. (2007)	Na-P1	48	150	0.5	0.06	
Shoumkova and Stoyanova (2013)	SOD	7	100	3-6	0.84	
Franus et al. (2014)	Na-X	24	75	3.0	0.33	

2.9.2. DHS using MW heating

In one study, a CFA with total amorphous content of 62% including anhydrite, magnetite, quartz, and mullite as the major crystalline phases was utilized for the synthesis of zeolite Na-A by Querol

et al. (1997). Both CH and MW heating methods were used at temperatures between 150°C and 225°C as well as alkali concentration in the range of 1.0 to 5.0 M. They used a multi-mode MW oven providing the greatest power of 1 KW. Synthesis times of below 30 min were reported for MW heating, while prolonged reaction times of around 98h were required in the case of CH. Various zeolitic compounds including tobermorite, hydroxysodalite, analcite, Linde type F, and Na-P1 were generated by adjusting different synthesis conditions. The maximum CEC of the zeolites synthesized by means of CH was roughly 3.1 meq/g, which was also reproduced by the MW heating.

In another study, philipsite was synthesized by both CH and MW heating methods using a Japanese CFA with the Si/Al ratio of roughly 2.4 (Fukasawa et al., 2018). A 2.45 GHz MW reactor as well as a conventionally heated vessel were used with PID controllers to monitor the reaction temperature. They reported that at least 15min was required to raise the temperature up to 100°C for the CH, while less than 3min is sufficient for the rapid temperature rise up in case of MW heating. They also observed a reduction in the crystal growth rate while an improvement in the nucleation using MW heating. Synthesis of philipsite using a mixture of rice husk ash (with roughly 90% amorphous silica) and CFA was also studied by Fukui et al. (2007).

They added 40 g of CFA to 1L NaOH 2.0 M solution and heated the reaction mixture in a conventional oven for 1h at 100°C. Next, the mixture was filtered to separate the solid residues followed by adding rice husk ash to 50 cm³ of the filtrate solution and 9h of heating the mixture by both CH and MW energy. The CEC of the specimen synthesized by adding the rice husk ash was improved with 80 mg/ g maximum capacity. They also observed the finer size distribution of the crystallites produced by means of the MW radiation. The formation of higher portion of sodalite phase in the case of MW heating was also reported. In both CH and MW heating synthesis,

the philipsite crystallization was promoted up to the first 1h, while the portion of sodalite was increased after 1h. This may be attributed to the conversion of philipsite to a more thermodynamically stable phase like sodalite at prolonged reaction times. The hypothesis was that the formation of hot spot zones due to the heating of the carbon content of the rice husk ash to elevated temperatures favored the sodalite formation. The conclusion was that the MW heating could prevail the formation of sodalite crystals over other meta-stable phases in the case of local hot spot zone presence.

Synthesis of the zeolite Na-A using a kitchen MW oven with the frequency and maximum power of 2.45 GHz and 600 W, respectively by Tanaka et al. (2008). They introduced a two-step process to convert a CFA with 50% amorphous content and Si/Al ratio of 2.76 to zeolite. In the first step, the dissolution of aluminosilicates from the CFA matrix occurred using MW radiation for 1h by refluxing the evaporated solution to keep the reaction mixture volume stable. A reduction in the concentration of the precursor amorphous aluminosilicates was reported indicating the dissolution of these phases over the pretreatment period. In the next step, the solid remaining was separated and with the aim of adjusting the Si/Al ratio, the Al source reagent was mixed with the filtrate. They reported that compared to the zeolite Na-A available on the market with the CEC of 5.50 meq/g, the experimentally synthesized product exhibited comparable CEC of 4.70 meq/g.

The combination effect of both CH and MW heating was also explored by Kim and Lee (2009). A high power (2 KW, 2.45 GHz) industrial MW reactor was used to zeolitize the CFA with Si/Al ratio of roughly 2.0. The experimental procedure was started by adding 0.5 Kg of CFA to the 1L NaOH solution of 5.0 M followed by heating the mixture for 1 to 8h using the combination of the CH and MW radiation. In the next stage, the NaAlO_3 was added to the filtrate to adjust the Si/Al ratio of the mixture. They reported lower amounts of aluminosilicates solubility in the reaction

medium for the conventional MW compared to the industrial one used in this study. They also observed an increasing trend in the aluminosilicates concentration up to the first 2h of treatment for both CH and MW radiation. This concentration kept increasing up to 5h of treatment for MW heating, while remained constant for CH after 2h. They conducted the main hydrothermal synthesis using three different routes after the pretreatment stage including the combination of CH and MW each for 60 min, separate CH for 60 min, and separate MW radiation for 60 min. It was observed that the removal efficiency of the toxic cations such as Zn, Cd, and Pb for the product synthesized by the combination method was superior to those of the zeolites synthesized by separate CH and MW heating. In a recent study, a source of waste stream originating from the Plasma Electrolytic Oxidation (PEO) process was used to convert a Canadian CFA to zeolite (Behin et al., 2014). In the first step, they dissolved a mixture of 2.0 g of the CFA and 1.80 g of the NaOH within 3 mL of the mentioned waste stream. After the addition of 3 mL of NaAlO₃ to the solution, the aging process at 20°C for 2h was conducted. A 2.45 GHz single-mode MW apparatus was then used to heat the aged mixture for various radiation time intervals. The promotion in the degree of crystallinity was attributed to the sufficient radiation time and power. They also confirmed that a single-mode MW could potentially reduce the energy required for the CFA conversion due to the directing of the electromagnetic wave with a specific phase shift compared to the conventional household MW ovens.

2.10. Successive fusion pretreatment and hydrothermal synthesis

2.10.1. Successive fusion pretreatment and CH

To convert CFA to zeolite, an initial step of pretreatment before the main hydrothermal reaction was conducted in a pioneering study by Shigemoto et al. (1993). The pretreatment step mainly involved the fusion at elevated temperatures for the mixture of the solid CFA with NaOH. In the next step, aging of the mixture was done by adding the fusion product to the distilled water. The

main advantage of this fusion pretreatment was to dissolve the resilient and slowly soluble phases within the CFA matrix including mullite and quartz. This is mainly attributed to the destruction of the CFA matrix due to the simultaneous effects of high alkalinity and elevated temperatures providing a large amount of aluminosilicates into the reaction mixture for further gelation, nucleation, and crystal growth. Due to the more solubility of the aluminosilicates in the fused CFA compared to the unfused CFA, the zeolite synthesis yield would be higher. They also reported that the fusion zeolites exhibited 10 times higher surface area compared to the DHS method. In addition, superior degree of crystallinity as well as CEC was observed for the products synthesized by fusion pretreatment (Molina and Poole, 2004). Table 2-5 summarizes the results obtained by some of the studies investigated the synthesis of zeolites using the successive fusion pretreatment and CH (In these studies fusion step occurred at temperatures between 550 and 600°C for 1 to 2h).

2.10.2. Successive fusion pretreatment and MW heating

In one study, the zeolitization of CFA using the MW radiation after an initial fusion pretreatment was studied by Bukhari et al. (2014). To synthesize zeolite Na-A, they fused 1.9 g of CFA and 2.1 g of NaOH for 2h at 550°C. In the next step, they mixed the fusion product with 20 mL of aqueous solution followed by adding 3 mL of NaAlO₃ solution. The final mixture was then exposed to the MW radiation by using a 2.45 GHz single-mode MW apparatus embedded with a reflux condenser at various powers and reaction times. The produced zeolite efficiently removed heavy metals including Cu, Cr, Ba, and V. They also reported that the degree of crystallinity of the product was remarkably affected by the radiation time and power.

2.11. Key parameters affecting zeolite synthesis

Several parameters could play key roles in the including the synthesis time, presence of ionic

Table 2-5. Summary of the studies investigated zeolitized CFA synthesis using successive fusion and CH methods

Studies	Type of zeolite	Conditions of dissolution			Conditions of crystallization		Remarks
		t (h)	T(°C)	NaOH (M)	t (h)	T(°C)	
Kazemian et al. (2010)	Na-P1	0.5	70	0.8	4	120	
Kumar et al. (2004)	Na-A	8	25		2	90	
Fotovvat et al. (2009)	Na-A, Na-X	8	25	2.7	12	100	
Rayalu et al. (2001)	Na-A	8			3	100	
Belviso et al. (2010)	Na-X	24	25		48	65	Sea water was used
Musyoka et al. (2013)	Na-X	2	25	6.0	9	80	Mine water was used
Klamrassamee (2010)	Sodalite	12	25	5.5	4	90	
Bergaut and Singer (1995)	Na-P1	12	25		6	100	
Izidoro et al. (2013)	Na-A	16	25	3.0	24	100	
Ruen-ngam et al. (2009)	Na-X	12	30	3.0	4	90	

species, heat source, alkalinity, and CFA composition. Some of these parameters are discussed in the following sections.

2.11.1. Synthesis time

Synthesis time is by far one of the most vital parameters affecting zeoliteization process through hydrothermal synthesis. The crystallization time could influence several zeolitic properties including the phase, crystallinity, and crystallite size (Nishiyama et al., 2009). Various researchers have investigated the impact of the reaction time and confirmed that prolonged synthesis times could result in larger crystallite sizes according to Ostwald ripening phenomenon (Oleksiak and Rimer, 2014; MiarAlipour et al., 2014). This law expresses that at longer synthesis times; the smaller crystallites are thermodynamically more unstable and could dissolve and attach to the

surface of larger particles. However, short crystallization times would result in a large amorphous content within the product declining the purity of the final zeolite.

The crystallization time influence on the phase purity, crystallite size, and crystallinity of the synthesized zeolites was studied by Askari et al. (2012). At 3h synthesis time, a broadened hump was observed in the XRD profile corresponding to the presence of the amorphous phase. At prolonged synthesis time of 14h, the target zeolite was produced without noticeable amorphous phase. Since the particle size is strongly affected by the synthesis time, monitoring this parameter to produce a zeolite with high crystallinity and surface area is of a paramount importance.

2.11.2. Alkalinity

As discussed earlier, the hydrothermal synthesis of zeolites starts by dissolving the aluminosilicates within the waste matrix into the reaction media. Since this dissolution strongly affects the conversion rate of CFA, the alkalinity of the reaction media could considerably improve the minerals dissolution rate. Increasing the pH of the reaction media could accelerate the quartz dissolution rate from the CFA matrix, while mullite is still resilient to dissolution at high pH (Rayalu et al., 2001). The formation of a specific zeolite type is triggered by the dissolution of these aluminosilicates. However, some studies observed the preferred formation of hydroxysodalite phase over other meta stable phases at higher pH (Murayama et al., 2002). This could be mainly attributed to the desirable conditions for the nucleation of hydroxysodalite at higher pH in the beginning of the crystal growth stage. Presence of OH^- ions, which is mainly accompanied by the presence of cationic species such as K^+ and Na^+ , is the main reason for increasing the pH of the reaction mixture. However, some studies confirmed different performance functions for both OH^- and Na^+ during the hydrothermal synthesis stages (Murayama et al., 2002).

2.11.3. Presence of ionic species

Similar aluminosilicate gels containing various alkali cations could produce different zeolitic structure types. The major determining parameter in the formation of a specific zeolite framework is the interaction of the metallic cations available and the soluble aluminosilicates (Bukhari et al., 2015). Since the cations could favor one framework over another, the alkali templates (such as NaOH or KOH) are also called “structure directing agents (SDA)” (Ali Zaidi and Rohani, 2005). The influence of K^+ and Na^+ species on the zeolitization of CFA was studied by Murayama et al. (2002). They dissolved 0.1 Kg of CFA within three different SDAs including Na_2CO_3 , KOH, and NaOH prior to heating the solutions at 100°C using a CH oven. They observed the preferred formation of zeolite Na-P1 in the solution containing Na^+ . The crystal growth rate, however; was declined at lower Na^+ concentration. They also reported that faster chabazite formation (3h) occurred for the combination of Na^+ and K^+ compared to the 24h in the case of K^+ solely. This increase in the crystallization rate could be ascribed to the impact of Na^+ on the solubility of aluminosilicates from CFA. Some studies have also observed the edingtonite formation in the presence of Cs^+ while the presence of Na^+ and K^+ could favor the formation of either zeolite Na-A or chabazite [88]. The crystal growth could also be monitored by the presence of different cations. So far, according to the literature, zeolites including hydroxysodalite, Na-philipsite, herschelite, and analcite have been produced within NaOH solution using CFA (Ríos et al., 2009). However, KOH as an SDA under identical synthesis parameters has produced zeolites such as Linde type-F, K-chabazite, and Barrer-KF.

2.11.4. Source of heating

In one study, pure chemical reagents were used to synthesize zeolites ZSM-5 and Y using both MW and CH (Arafat et al., 1993). They reported that the MW radiation synthesized zeolite Y just in 10 min, while in the case of CH prolonged synthesis time of 10 to 50h was required. On the

other hand, CH needed couple of days to synthesize ZSM-5, while 30 min radiation was sufficient to produce ZSM-5 of high crystallinity. Higher nucleation rate as well as faster dissolution rate of aluminosilicates could be the major causes of rapid crystal growth using novel MW energy. In another study, zeolite Na-A was synthesized from pure chemicals using a 2.45 GHz single-mode MW apparatus by Bukhari et al. (2014). They reported that the product degree of crystallinity was considerably influenced by the MW radiation power and time. They also observed a favored formation of zeolite Na-A over Na-X at higher power of radiation. In the case of MW heating, the nucleation occurs more rapidly resulting in a slower crystal growth rate. Apart from much faster nucleation rate, a greater dissolution of the aluminosilicates from the CFA matrix could be achieved using the MW radiation (Kim and Lee, 2009; Inada et al., 2005). Nevertheless, the aluminosilicates concentration within the hydrous gel with gradual progress in the reaction will ultimately reach an equilibrium. The scanning electron microscope images revealed that the zeolitization of aluminosilicate-based wastes is a heterogeneous phenomenon since the crystals grow on the surface of the amorphous CFA particles (Kazemian et al., 2010). After the crystal formation, the zeolitic layers on the CFA surface would trap the residual aluminosilicates in a way that they could be out of the reaction accessibility (Kim and Lee, 2009). Moreover, the CFA particles with higher surface area potentially provide more soluble aluminosilicates resulting in higher zeolite crystallization degree.

2.11.5. Seeding

To prepare a pure zeolitic compound, seeding is a great contributing technique (Zhao et al., 1997). Since zeolites are metastable crystalline phases, in a hydrothermal process there is likely to synthesize a combination of multiple phases. Hence, synthesis of a desirable phase requires the optimization of the synthesis parameters. Leading the reaction towards the synthesis of a specific zeolite framework could also be conducted by seeding action. Aluminosilicate gel slurries as well

as synthetic and natural zeolites could also be used for seeding purpose. In one study, Zhao et al. (Zhao et al., 1997) synthesized pure zeolite Y without undesirable by-products from CFA using aluminosilicate gel slurry as seed material. Favoring the formation of one phase over another due to the seeding action has also been reported in several studies (Zhao et al., 1997; Wu et al., 2006). The effects of seeding and aging on the synthesis of zeolite Na-A from CFA using both CH and MW radiation was studied by Slangen et al. (1997). The preliminary solutions were aged ranging from 10 to 1200 min followed by heating the mixtures using a household MW and CH ovens. In the case of CH, pure zeolite A was produced within 12h while MW radiation required roughly 1 min to synthesize the similar compound. They also observed that mixing the unaged and aged samples produced the zeolite A with higher degree of crystallinity. Hence, aging the specimens prior to the main crystallization step could remarkably contribute to the zeolite synthesis yield (Slangen et al., 1997). In another words, the large amounts of nuclei formed over the aging period in the aged specimen could act as seeds for the crystal growth within the unaged specimen.

2.12. Tobermorite

Tobermorite was first discovered in 1880 by an Scottish mineralogist in Tobermory, Scotland from where it obtained its name. Due to the structural similarities with the calcium silicate hydrate (CSH) binder in the hydrated cement paste, large attention has been focused on the broaden study of this mineral microstructure (Richardson et al., 2004; Jennings et al., 2007). The applications of tobermorite as potential adsorbents for the removal of contaminants and seeds for the growth of CSH binder within the cementitious matrix have been reported by several studies (Land and Stephan, 2015; Berg et al., 2006). Within the cavities of porous rocks, prolonged contact of the granite and limestone will naturally result in the crystallization of tobermorite within a geothermal hyper-alkaline environment. In another words, the complicated synthesis condition required to

precipitate a noticeable mass fraction of pure tobermorite crystallites is likely to be the main reason of the recent controversies over the precise refinement of its microstructure.

The overall structure of the tobermorite consists of main central CaO sheets, which are flanked on both sides by silicates tetrahedral long polymeric chains (Berg et al., 2006, Jennings et al., 2007). Having three hydration degrees, natural tobermorite has been observed with mainly planar or fibrous morphologies. The interlayer spacing of the adjacent layers could vary from 9Å, to 11Å and 14Å according to the water content within the basal spacing. This would give rise to three main tobermorite microstructures including 9Å, 11Å, and 14Å tobermorites out of which 11Å is reported to be the most stable within the ambient environment (Richardson et al., 2004, Andersen et al., 2004). The major distinctions in the microstructure of these polymorphs are discussed in the following sections.

2.12.1. Tobermorite microstructure

2.12.1.1. 11Å polymorph

Compared to the 9Å tobermorite, the 11Å polymorph exhibits a more complicated structure as it has two classes in terms of their structural behavior after the dehydration of the interlayer spacing water. This could also be the reason why the exact composition of the 11Å tobermorite is still unknown. In one of the classes, the interlayer spacing shrinks to the 9Å type upon dehydration at 300°C, which is called “normal” 11Å tobermorite. In the other case, the interlayer spacing would maintain its basal spacing upon dehydration at 300°C, which is called “anomalous” 11Å tobermorite (Mitsuda and Taylor, 1978; Bell et al., 1996).

Due to the remarkable structural disorder and poor crystallinity, the precise resolving of this mineral structure would be a complex phenomenon. McConnel (1954) did the pioneering investigation on determining the crystallographic parameters of the 11Å tobermorite. He collected

a normal 11Å tobermorite specimen from Northern Ireland and specified the unit cell geometry as orthorhombic. He also showed that with some structural defects in between, the growth of the layered structure preferentially occurs along with c axis. The main compositions for the 11Å tobermorite recommended by him was either $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 5\text{H}_2\text{O}$.

Shortly after, another study was conducted by Megaw and Kelsey (1956) using a sample from the same location. They also described the 11Å tobermorite as an infinite set of adjacent layered structures containing central CaO sheets with an orthorhombic crystal geometry and composition of $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Long polymeric chains of silicates with a “dreierketten” structure have also attached to the main CaO sheets on both sides. The water molecules and cations such as Ca^{2+} , Na^+ , and K^+ occupy the interlayer spacing of the adjacent layers. The schematic representation of the layered microstructure and the dreierketten arrangement of the silicate chains within the 11Å tobermorite is illustrated in Figure 2-5.

Some studies have also focused on the microstructural distinctions between the anomalous and normal 11Å tobermorite. Mitsuda and Taylor [99] reported that the silicate chains are connected to the central CaO sheets only in the anomalous polymorph. However, another study attributed this distinction solely to the Ca zeolitic ions availability within the interlayer spacing of the normal type and confirmed the connectivity of the silicate chains to the CaO sheets in both polymorphs (Merlino et al., 2001). They reported that these zeolitic cations in the normal type are connected to the water molecules within the interlayer spacing, which over the dehydration period could be evaporated. The shrinkage of the 11Å to the 9Å tobermorite will then occur, while the exact mechanism of this shrinkage is still unknown. It was also confirmed in this study that the presence of the mentioned zeolitic ions within the cavity of the normal type could slightly change the composition of the normal and anomalous polymorphs (Merlino et al., 2001).

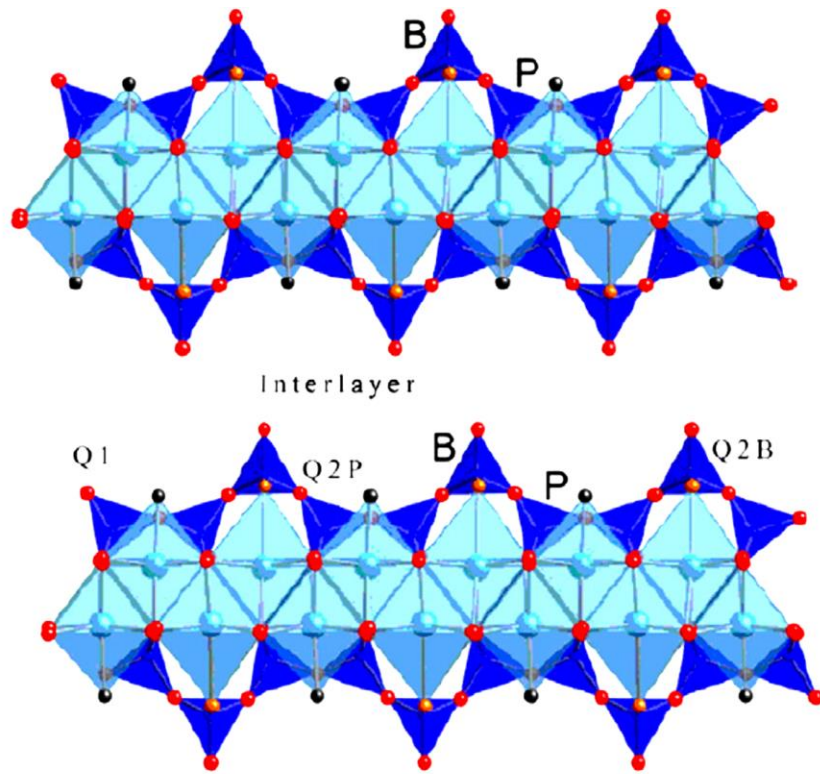


Figure 2-5. Schematic illustration of the the layered microstructure and the dreierketten arrangement of the silicate chains within the 11Å tobermorite. In this graph, the pairing and bridging tetrahedral are shown by Q2P and Q2B, respectively. The end chain silica tetrahedral are described as Q1. The dark blue represents silica tetrahedral and light blue represents the CaO sheets (Lothenbach and Nonat, 2015)

The presence of a third 11Å tobermorite family polymorph called “clinotobermorite” has also been reported by Merlino et al. (2001). This polymorph is quite similar to the normal type in terms of the zeolite cations and structure. The main difference reported was regarding the unit cell geometries that the normal type has a monoclinic while the clinotobermorite possesses both triclinic and monoclinic configurations. Similar to the normal type over the dehydration period, this polymorph also shrinks to 9Å upon 300°C. The recommended composition for this polymorph is $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$ (Merlino et al., 2001).

2.12.1.2. 14Å polymorph

This polymorph with the recommended composition of $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ and the highest water content in the interlayer spacing is also called “plombierite”. Similar layered structure as the one discussed in Figure 5 has also been proposed for the 14Å type consisting of the central seven-fold CaO sheets flanked on both sides by long chains of dreierketten-arranged silicate tetrahedral. The interlayer spacing of the layered microstructure has been occupied by the zeolitic ions as well of water molecules likewise to the 11Å polymorph. This type with a monoclinic unit cell geometry tends to shrink to the 11Å type upon dehydration occurs at temperatures ranging between 80 to 100°C. This indicates the more structural instability of the 14Å type compared to the 11Å mainly due to the larger interlayer spacing (Merlino et al., 2001).

2.12.1.3. 9Å polymorph

Generally the dehydration occurs upon the 300°C would result in the formation of the 9Å polymorph due to the shrinkage of either clinotobermorite or the normal 11Å type. Similar structural configuration discussed in the previous sections is also available in this polymorph. However since the 9Å is the lowest hydrated type, the CaO sheets clamped on both sides by the dreierketten-arranged silicate chains have slightly narrower spacing. Out of the five water molecules within the interlayer of the 11Å type, one is in coordination with the Si-OH bonds in the surface of the silicate chains while the other four molecules are lost during the dehydration of the 11Å to the 9Å (Merlino et al., 2001). The zeolitic Ca ions are similarly to the other two polymorphs resident in the interlayer of the 9Å tobermorite with the recommended composition of the $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$.

2.12.2. Al-substituted tobermorite

The partial substitution of the silicate tetrahedral especially with Al and in some other cases with other cations including Na, Fe, and Mg within the tobermorite microstructure has also been reported in some studies (Jakobsson and Moore, 1986). The naturally occurred tobermorite has a more chance to be found in the Al-substituted form compared to the simple non-substituted form, even though it has also been synthesized in the lab-scale. Several pioneering studies have investigated the substitution capacity and changes that occur to the structure due to the substitution of the Al within the silicate dreierketten chains. Some studies have observed the higher stability in the case of tobermorite substituted with Al compared to the one without Al, which transformed to xonotlite under particular synthesis conditions (Sakiyama and Mitsuda, 1977; Gabrovšek et al., 1993).

The Al involvement within the layered tobermorite microstructure has been a matter of debate by many researchers. Depending on the target position of substitution, Al could be observed with various coordination numbers ranging from pentahedral for the replacement with the zeolitic Ca to tetrahedral for the replacement with the silicate tetrahedral of the dreierketten chains (Kalousek, 1957). However, the majority of the Al substitution observed within the tobermorite structure has been ascribed to the replacement with the dreierketten chains silicates. Different studies have also traced the target positions for the Al substitution within the silicate polymeric chains as well. The majority of them have confirmed that it is unlikely for the Al to be substituted in the silicate end chain sites, while the branching and bridging sites are the most desirable target sites (Guo et al., 2017). Figure 2-6 illustrates different preferred Al substitution sites within the tobermorite layered structure according to a model described by Geng et al. (2017).

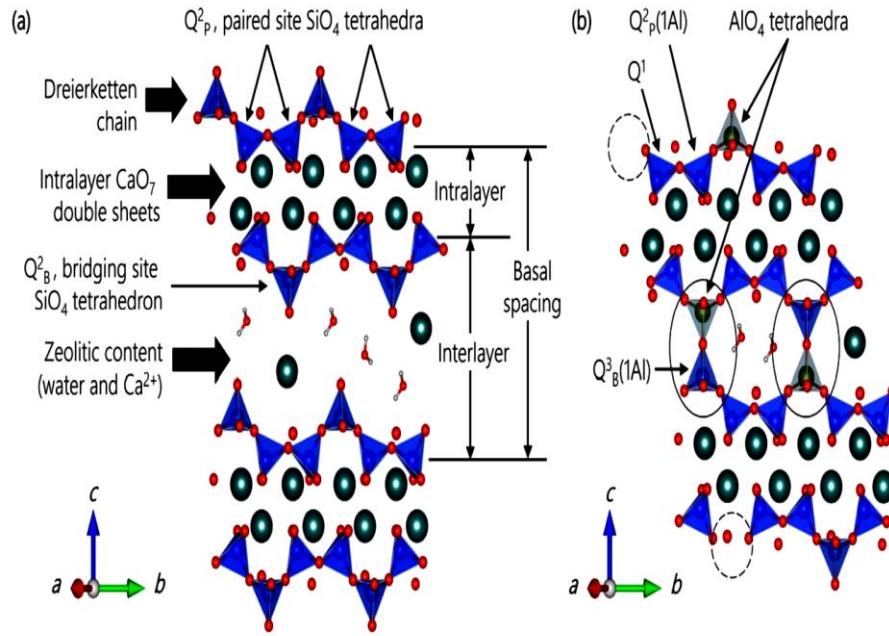


Figure 2-6. Schematic illustration of a) non-substituted and b) Al-substituted layered tobermorite structure with Al substitution at bridging and branching sites. The white, red, blue, black, and green spheres represent H, O, Si, Al, and Ca, respectively (Geng et al., 2017)

Several studies have confirmed that Al/(Si+Al) molar ratio of 0.15 is an optimum value to prepare a stable tobermorite layered structure by partial substitution of Al within the microstructure (Shaw et al., 2000; Wang et al., 2017). The by-products formation including hydrogarnet (a type of calcium aluminosilicate hydrate) has been reported at ratios above 0.15 [108]. Magnesium, iron, and sodium are the other ionic species that could interact with the layered tobermorite microstructure apart from aluminum (Wang et al., 2017). After the deprotonation of the SiOH groups, the Na⁺ ions could be substituted into the positions of H⁺ and counterbalance the net negative charge on the surface of the layered tobermorite. This will provide the Na substituted tobermorite with remarkable ion exchange CEC for the removal of toxic metals such as lead and cesium (Coleman, 2011; Coleman et al., 2014).

The net negative charge of the surface within the tobermorite layered structure could also be counterbalanced by the interaction of other alkalis including Br and/or K (Coleman et al., 2014). It has been reported that Ca ions could overcompensate the mentioned negative surface charge due to their larger ionic size, hence; be more preferred in the interlayer spacing compared to the alkalis like Na and K (Labbez et al., 2007). However, the preferable uptake of Ca instead of Na in the interlayer spacing could decline the cesium removal efficiency as this toxic cation has a more tendency to be exchanged with Na (Lothenbach and Nonat, 2015). Therefore, the remediation of radioactive wastes as well as nuclear plant circulating water could be remarkably improved by this selection in cesium exchange.

The divalent heavy metals including Zn^{2+} , Cd^{2+} , Ni^{2+} , and Co^{2+} , on the other hand, have a great affinity to be exchanged with the Ca ions present in the interlayer spacing of the layered tobermorite structure (Coleman et al., 2014). Tobermorite could also be applied to decontaminate the phosphates and heavy metals from the polluted waters (Coleman, 2011). In the case of phosphate removal, hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) is generated and covered the surface of the interlayer spacing resulting in the capture of phosphates and the water cleanup.

2.12.3. Crystalline phases hydrothermal stability within systems containing CaO-SiO₂-H₂O

With above forty crystalline phases, the CaO-SiO₂-H₂O system could be remarkably complicated with a broad range of species exhibiting a huge variety of compositions and structures. The formation of these complicated structures could be ascribed to the different coordination of the Ca and O atoms due to the Ca electropositive nature (Hamid, 1979). Even though CH hydrothermal treatment could synthesize the majority of these minerals, monitoring the reaction parameters is of a paramount importance as these factors may favor the formation of one phase over the other. Some of the main synthesis parameters including the reaction time, temperature and Ca/Si molar

ratio. Hence, synthesis of a single-phase mineral with high crystallinity and purity through such system could be too difficult. This could make the detection of these phases complicated.

Truscottite, gyrolite, tobermorite, and xonotlite are the major phases that gained attention in terms of the hydrothermal stability in several studies (Shaw et al., 2000, Bonaccorsi and Merlino, 2005). The tobermorite to xonotlite transformation has been extensively studied in the literature. However, the exact mechanism of this change has been a matter of debate since the proper tracking of this change requires the consideration of several parameters (Black et al., 2003). García et al. (2018) in their investigation by keeping the Ca/Si molar ratio constant at 1, observed 160°C as the minimum temperature required to transform tobermorite to xonotlite. Temperatures close to 185°C, however; was reported for the transformation of a well crystalline tobermorite to xonotlite. In another study, the estimated temperature range for the tobermorite to xonotlite transformation was reported to be 170°C with the deviation of $\pm 20^\circ\text{C}$ by Claverie et al. (2019). Wu et al. (2020) directly correlated the Ca/Si ratio to the tobermorite thermal stability and observed the higher thermodynamic stability of tobermorite with Ca/Si ratio of 0.8 compared to the phase with 1.0. They also investigated the impact of high pressures on the thermal transformation of tobermorite to xonotlite and reported that tobermorite is more thermodynamically stable at elevated temperatures and pressures. Zou et al. (2016) investigated thermal stability of tobermorite fibers and found that at temperatures beyond 140°C transformation to xonotlite occurred, while at temperatures less than 100°C virtually amorphous CSH was obtained.

The impact of partial Al substitution with silica tetrahedral on the thermal stability of tobermorite was also studied by Shaw et al. (2000). They conducted a detailed investigation of kinetic parameters in temperatures between 235°C and 310°C and recommended a mechanism for tobermorite formation. At ambient temperature, an amorphous CSH gel was formed followed by

an introduction of periodicity in the gel and ultimately crystal growth of tobermorite. To minimize the by-products formation including xonotlite, precise monitoring of temperature is highly demanded due to the system instability at elevated temperatures. The major reason for higher stability of xonotlite compared to the tobermorite is attributed to the distinctions within their microstructure. The layered tobermorite structure consists of interlayer spacing containing water molecules, while there is no such interlayer in xonotlite structure (Zou et al., 2016). Hence, xonotlite is more thermodynamically stable at elevated temperatures.

To summarize, considering the boundary of phases and variety of the synthesis parameters the CaO-SiO₂-H₂O system could be very complicated. Therefore, precise detection of the conditions at which a specific phase is stable is too difficult a task due to the large variability of the parameters controlling the system.

2.12.4. Tobermorite hydrothermal synthesis

Due to the lack of information regarding the 14Å tobermorite synthesis in the literature, this section is dedicated to the 11Å tobermorite hydrothermal synthesis. In the case of 9Å, this polymorph could be simply obtained by shrinkage of the 11Å type due to the dehydration upon 300°C. Hence, hydrothermal synthesis of this polymorph has not been reported. The temperature ranges at which tobermorite is stable could be narrower rather than xonotlite due to the higher stability of xonotlite, according to the discussion in previous section.

Over the recent years considering many distinct synthesis procedures, huge pioneering efforts have been made to synthesize pure well crystalline 11Å tobermorite. Understanding the phase boundaries of tobermorite/xonotlite as well as the impact of Al substitution on the stability of 11Å tobermorite were the main topics of investigation. As mentioned earlier, variability of the monitoring parameters makes it complicated to obtain clear optimum conditions for the purpose of 11Å

tobermorite synthesis with high purity and crystallinity. The influence of various parameters including temperature, reaction time, Ca/Si ratio, precursors, partial Al substitution, and alkalinity on the reaction kinetics was explored in most studies.

Various precursors effects such as Ca-formate, sucrose, borosilicate, and EDTA on the 11Å tobermorite synthesis were investigated (Huang et al., 2003; Tränkle et al., 2013; Hartmann et al., 2014; Hartmann and Buhl, 2010). Utilization of other precursors such as Na₂SiO₃, calcsilicate alkoxide gel, and Ca(NO₃)₂ has also been reported, even though SiO₂ and CaO have been used as the most common precursors (Lin et al., 2006). The application of some silico-calcareous waste by-products including paper recycling residues, cement kiln dust, oil shale ash, and blast furnace slag has also been reported in many studies (Reinik et al., 2011; Nakahira et al., 2008). The pulverizing of the precursors prior to the main crystallization step was conducted in several studies (Bonaccorsi and Merlino, 2005; Coleman et al., 2011). Using the temperatures mainly above 200°C, prolonged synthesis times from couple of hours to months applied to synthesize 11Å tobermorite. Different studies have reported various values for the optimal synthesis parameters to obtain pure well crystalline 11Å tobermorite resulting in a broad contradiction in the literature. For instance, 11Å tobermorite synthesis at 140°C with the Ca/Si ratio of 0.8 was conducted in 60h using quartz and CaO in a study by Hamid (1979).

However, under identical precursors and synthesis parameters Speakman (1968) produced 11Å tobermorite within 196 days. An effort was made by Kalousek et al. (1957) to explore the synthesis conditions at which pure 11Å tobermorite is stable. To consider the impact of Al substitution, they adjusted the Ca/(Si+Al) at 0.8 and conducted the hydrothermal reaction at 175°C for 24h within the initial step. They observed that higher Al contents resulted in a mixture of katoite (a type of calcium aluminosilicate hydrate) and 11Å tobermorite, while lower Al contents provided pure 11Å

tobermorite. They conducted the hydrothermal synthesis for 72h at 170°C with Ca/(Si+Al) fixed at 1.0 in the second step. This time, a mixture of hydrogarnet ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$) and 11Å tobermorite was obtained. Temperature of 170°C, reaction time of 15h, and Ca/(Si+Al) of 1.0 were the synthesis conditions for their final set of hydrothermal treatment. They approved that under 12%, Al substitution would contribute to the stability of the 11Å tobermorite, while above that amount by-products formation was observed.

In another study, Mitsuda et al. (1978) investigated the impact of the silica precursor. To obtain this target, clinoptilolite, aluminosilicic gel, and colloidal SiO_2 were the several precursors they utilized for the synthesis purpose. Two Ca/(Si+Al) ratios of 1.0 and 0.8 were used for each individual precursor studied. The synthesis was conducted at two temperatures of 120°C and 90°C while different Al% between 0% and 15% based on composition ratio were used. They observed that highly stable 11Å tobermorite was obtained at lower Al contents. They also reported that in the case with Ca/(Si+Al) ratio of 1.0, the tobermorite layered structure was less stable compared to the case with the ratio of 0.8. Accelerated crystallization of tobermorite was facilitated at elevated temperatures. The results also showed that the utilization of aluminosilicic gel prepared tobermorite with higher purity and degree of crystallinity compared to the other sources.

Different synthesis parameters including water/solid ratio of 5, temperature of 120°C, several reaction times, and Ca/(Si+Al) ratio of 0.8 were used to explore the impact of silica precursor in a study by Grangeon et al. (2016). Colloidal silica fume, silicic acid, and quartz were the various starting sources, which were studied in this work. Short synthesis time of 4h was sufficient to obtain highly crystalline tobermorite in the case of quartz. However, prolonged reaction times of 24h for the colloidal silica fume, and 8h for the silicic acid were required for the synthesis of tobermorite with relatively lower degree of crystallinity compared to quartz.

The synthesis of normal and anomalous polymorphs was also studied thoroughly by El-Hemaly et al. (1977). Even though they conducted detailed experiments on the of 11Å tobermorite synthesis, the precise conditions at which one polymorph is favored over the other have not been clearly reported. Several types of precursors have been utilized including cristobalite, quartz, and colloidal silica. The impact of alkaline reagents and alumina was also studied under the reaction conditions following 2h to 14 days of reaction time at 120 to 180°C. In terms of morphology, the most commonly observed are either fibrous or platy-like. Applying some reaction parameters modifications could potentially result in fibrous morphology, even though the majority of the studies have observed the platy-like one. The impact of the reaction medium pH on the morphology of the resultant tobermorite using Ca-EDTA complex as precursor has been studied by Huang et al (2003). They found that platy-like morphology was obtained at lower pH, while at pH around 13 fibrous morphologies have been observed.

2.12.4.1. CH and MW-assisted hydrothermal synthesis of 11Å tobermorite

Various silica sources have been used by different researchers to synthesize 11Å tobermorite hydrothermally which has taken synthesis time from at least several hours up to several days by means of CH. Reagent-grade chemicals including CaO, fumed silica, aluminum nano-hydrate were used by Gauo et al. (2017) to synthesize Al-substituted 11Å tobermorite via CH. Based on the ideal tobermorite composition, the Ca/Si ratio of the non Al-substituted sample was adjusted at 0.83. The water/solid ratio was kept constant at 10.0 while the molar ratio of Ca/(Si+Al) adjusted at 0.83 for the Al-substituted sample. Prior to being put within an autoclave vessel for the main hydrothermal synthesis, the slurry was properly mixed. The synthesis was conducted at 1 Mpa saturated steam pressure and 180°C. The reaction times for both Al-substituted and Al-free samples

were set at 1h, 3h, 5h, 9h, and 24h. Synthesis time of 5h was found as the optimum value for both Al-substituted and Al-free samples.

The removal of Sr^{2+} and Cs^+ using an Al-substituted 11Å tobermorite synthesized from blast furnace slag using CH method was also reported by Tsutsumi et al. (2014). In the first stage, the pulverization of slag was conducted for 4h using a ball milling equipment. Then the slag powder was well mixed with NaOH and sodium silicate in 15 cm³ of DI water with initial Ca/(Si+Al) adjusted at 0.83. The synthesis was conducted for 2-48h at 180°C within a sealed autoclave vessel. A noticeable selectivity for the removal of Sr^{2+} and Cs^+ was observed for the Al-substituted 11Å tobermorite sample synthesized after 48h of hydrothermal treatment. In another study, a mixture of K-feldspar powder and chemical grade CaO was converted to the Al-substituted 11Å tobermorite using CH hydrothermal method by Yang et al. (2015). The K-feldspar powder was firstly ground and then mixed with CaO and distilled water to adjust the initial Ca/(Si+Al) at 0.83. The mixture was then hydrothermally treated at 180-250°C for 4-8h. Reaction temperature of 250°C and 48h of reaction time was found sufficient for the synthesis of well crystalline tobermorite.

Trankle et al. (2013) also reported the CH versus MW-assisted hydrothermal synthesis of 11Å tobermorite. In their study, defined amounts of various silica sources including silicic acid, quartz, and borosilicate glass and 0.365g of $\text{Ca}(\text{OH})_2$ were mixed with 120 mL of DI water within a sealed vessel to adjust the Ca/Si ratio within the range of 0.36-1.78. The synthesis was conducted for 7days at 200°C within an oven at which the slurry was rotated for proper mixing. For the MW-assisted synthesis experiments, 50 mL of DI water, a certain amount of Si sources, and 0.148g of $\text{Ca}(\text{OH})_2$ were properly mixed and transferred into a sealed vessel that was then exposed to MW

radiation at 200°C for 8h. Eventhough, the 11Å tobermorite prepared by means of CH exhibited greater crystallinity, MW radiation provided a faster formation of crystalline 11Å tobermorite.

2.13. Conclusions

The global ever-increasing amount of aluminosilicate-based wastes such as WG cullet and CFA has become a serious environmental concern, while landfilling could not be an environmentally friendly option. This could be attributed to the non-biodegradable nature as well as the presence of toxic elements within the composition of these wastes. Hence, the best strategy for the green recycling of these wastes is their conversion to highly value-added products such as zeolites and tobermorites. Due to their excellent thermochemical stability and shape selectivity, zeolites have found broadened applications as ion exchangers, molecular sieves, and catalysts for petrochemical, environmental, and industrial sectors. Synthesis of high CEC zeolites from CFA has gained a remarkable attention due to their great contribution to the heavy metals removal from industrial and domestic contaminated water sources. High CEC zeolites were obtained combining both the CH and MW-assisted hydrothermal synthesis. In order to synthesize materials with properties suitable for a broaden application ranges; the influences of these sources of energy should be further explored.

The zeolitization of the aluminosilicate-based wastes such as CFA is too complicated and finding the clear mechanism still requires more investigation. However, remarkable efforts have been made to thoroughly examine the impact of variable reaction parameters monitoring the zeolitization process. The main influencing factors including but not limited to aging time, concentration and type of the template, synthesis procedure, source of energy, alkalinity, type and concentration of the waste, seeding, and Si/Al ratio.

Having discussed the results obtained by many studies focused on promoting the zeolitization of CFA using novel MW radiation, the current research aims to perfect this method by conducting further detailed experimental work. Target zeolites have been produced more efficiently by means of MW radiation due to the acceleration of the synthesis kinetics. Due to faster temperature rise up and faster nucleation rate, MW heating was found to be remarkably effective on reducing the crystallite size and increasing the degree of crystallinity. Aluminosilicates dissolution rate could also be improved using MW heating; thus shortening the reaction time considerably.

The structural similarities between the 11A° tobermorite and CSH gel has also been discussed in this chapter. Using specific hydrothermal synthesis parameters, tobermorite and xonotlite phases have mentioned to be closely related in terms of their thermodynamic equilibrium, composition, and structure. A thorough description of the compositional as well as structural relationships between different tobermorite polymorphs was provided prior to the hydrothermal synthesis section. Tobermorite-like CSH phases are synthesized within a system with a complicated behavior and refining their structures still require further investigation in most cases. For instance, there is still a great controversy over the structural distinctions between the normal and anomalous 11A° tobermorites and the mechanism through which one polymorph is favored over the other is still ambiguous. A thorough literature review over the recent advancements in the 11A° tobermorite hydrothermal synthesis was also provided in this chapter. Even though significant research efforts have been made to clarify the synthesis conditions at which tobermorite structure could exhibit the most hydrothermal stability, no study has reported a precise set of optimal conditions for the stability. Due to the considerable meta stability of the system, synthesis of pure highly crystalline tobermorite without by-products formation is too difficult a task. Hence, finding the mechanism of tobermorite transformation to more thermodynamically stable phases such as

xonotlite plays a key role in understanding the precise system behavior as the information available in the literature is very controversial.

Chapter 3. Rapid zeolite synthesis from waste glass cullet using energy efficient microwave radiation *

Type of experiment	Scientific contribution
Microwave/Conventional heating synthesis	A.R. Majdinasab conducted all the synthesis experiments using microwave and conventional heating techniques.
XRD	A.R. Majdinasab prepared the samples and P.K. Manna from the Department of Physics and Astronomy did the data collection.
SEM/EDX	A.R. Majdinasab prepared the samples and A. Khan from the Manitoba Institute of Materials (MIM) did the data collection.
FTIR	A.R. Majdinasab prepared the samples and did the data collection.
TGA	A.R. Majdinasab prepared the samples and Y. Wroczynskyj from the Department of Physics and Astronomy did the data collection.

*This chapter has been published as: Majdinasab, A. R., Manna, P. K., Wroczynskyj, Y., van Lierop, J., Cicek, N., Tranmer, G. K., & Yuan, Q. (2019). Cost-effective zeolite synthesis from waste glass cullet using energy efficient microwave radiation. *Materials Chemistry and Physics*, 221, 272-287.

This chapter was fulfilled with the main objectives including: a) synthesis of value-added zeolites from cheap and readily available waste glass precursors by means of rapid microwave radiation and comparing the properties in terms of degree of crystallinity, crystallite size, and type of the phases with those synthesized by means of conventional heating; and b) providing a thorough comparison between constant temperature /constant power microwave radiation modes in terms of energy consumption, and their impact on the nucleation, and degree of crystallinity.

The results obtained in this chapter contributed to the main objectives as they showed that microwave radiation was a fast and efficient technique that remarkably reduced the crystallization time from prolonged hours in conventional heating to couple of minutes with comparable crystallinity and water holding capacity. This chapter further contributed to the main objectives by suggesting the best microwave radiation conditions at which the least energy consumed and the highest crystallinity of products obtained using constant temperature radiation. This chapter also suggested a promising option to modify the configuration of the microwave reactor to improve the nucleation rate and crystallinity using constant power radiation mode.

Abstract

A rapid zeolite synthesis procedure was investigated using pulverized waste glass cullet via microwave radiation and compared with zeolites synthesized using convection heating. It was observed that constant temperature microwave synthesis method made zeolites more efficiently under superheating conditions with a maximum relative crystallinity of 60%. The maximum relative crystallinity of the synthesized zeolites was found to be similar when convection heating and constant temperature controlled microwave synthesis was used; however, the latter technique offered a factor of 140 reduction in synthesis time. This rapid synthesis process is attractive to the industrial application due to its high-energy efficiency.

3.1. Introduction

Zeolites are natural, hydrated aluminosilicate minerals that belong to the tectosilicates mineral type and possess very small regular internal cavities (<2 nm) with crystalline microporous frameworks. These porous materials are extremely useful in a number of industrial applications such as water and gas sorption, water filtration, and as soil fertilizers (Nabavi et al., 2014). Apart from the traditional procedures of zeolite synthesis via pure chemical reactions, a large number of alternative materials have been employed as starting precursors for the synthesis of zeolites using alkaline hydrothermal reactions. Out of these, various aluminosilicate-based waste materials such as paper sludge ash, rice husks, and coal fly ash have been utilized to synthesize zeolites (Wajima et al., 2004; Dey et al., 2012; Shoumkova and Stoyanova, 2013a; Bac et al., 2010; Kuwahara et al., 2008; Cardoso et al., 2015; Behin et al., 2014; Musyoka et al., 2013). Using waste materials as the starting reagent for the synthesis of zeolites may have risks, particularly when incineration residuals like fly ash are utilized as the residuals could contain toxic elements such as Cd, Pb, Hg, Cr (VI), and As (Bukhari et al., 2015). On the other hand, using pure chemicals can be cost prohibitive for certain applications, making the zeolitic products not viable for agricultural and

environmental applications. Therefore, new cost-effective alternatives are desired for the synthesis of clean zeolites to satisfy the large demand for zeolitic materials.

Waste glass (WG) cullet procured from beverage bottles is predominately free of the potentially hazardous elements, and is broadly and conveniently accessible via separate collection systems of municipal solid wastes. Today, a majority of the collected WG is being recycled using processes that comply with economic and environmental aspects, but these conversion processes require extremely high temperatures (up to 1600°C) depending upon the glass composition (Felismina et al., 2017). As a result, high-energy consumption and greenhouse gas generation are the main drawbacks of WG recycling. Therefore, a large proportion of WG still goes to the landfill due to its high recycling costs. The best solution for this problem is to convert WG cullet to high value-added products such as zeolites. WG cullet from beverage bottles is suitable for the synthesis of zeolites since its major component is silicate, which is the main precursor of the starting gel.

The conversion of WG into zeolites can be done using a hydrothermal reaction involving digestion and dissolution, condensation, nucleation, and crystal growth (Shoumkova and Stoyanova, 2013b; Bukhari et al., 2014). This reaction occurs at high temperatures provided by convection heating (CH) techniques. Recently, a few studies have focused on zeolite synthesis using different WG sources such as TV LCD panels, windshield WG, and beverage bottles via CH (Kim et al., 2015a; Tsujiguchi et al., 2014a; Terzano et al., 2015). Over the last few years, use of microwave (MW) and ultrasound as alternative energy sources for the synthesis of porous materials has emerged due to the impact on induction periods and nucleation (Gordon et al., 2012; Sabouni et al., 2010; Chindaprasirt et al., 2013). It has been reported that MW radiation improves the nucleation stage bottleneck by reducing the induction period (Chindaprasirt et al., 2013).

The heat generation using microwave radiation typically occurs due to the interaction of dipolar molecules with MW radiation resulting in dielectric heating of the solution. Dielectric heating occurs when dielectric molecules follow the oscillations of an alternating electromagnetic field (Bukhari et al., 2015a). The energy dissipates in the form of heat via molecular friction leading to a volumetric distribution of heat compared to CH (Li and Yang, 2008). The application of MW radiation for the synthesis of zeolites offers several advantages over CH, including shortening of the crystallization time, generating narrower size distributions, eliminating undesirable phases, acceleration of nucleation processes, and producing various morphologies (Cundy and Zhao, 1998; Katsuki et al., 1999; Madhusoodana et al., 2006). Furthermore, non-thermal effects have also been reported. It has been confirmed that MW radiation elevates the normal boiling point of the solution due to the vessel being pressurized. This results in the nucleation retardation of gas vapors in the solution medium, which is broadly known as a “super heating” effect (Madhusoodana et al., 2006).

According to the previous studies, the reaction time reduction using MW radiation could be a consequence of a rapid uniform heating of the reaction mixture (Chindaprasirt et al., 2013; Madhusoodana et al., 2006). This causes more abundant nucleation at minute hot spots (Slangen et al., 1997; Bonaccorsi and Proverbio, 2003). Synthesis of zeolites and nanozeolites via MW heating using different precursors has been reported in recent studies. Bukhari et al. (2015b) synthesized zeolite Na-A from sodium aluminate and sodium silicate using a single-mode microwave reactor operating at atmospheric pressure. It was observed that the crystallinity of the synthesized product was affected by both the power and time of irradiation and single-phase zeolite Na-A was obtained with a crystallinity of 80% at 300W. Fukasawa et al. (2017) hydrothermally treated coal fly ash with NaOH solution using a MW heating reactor equipped with zirconia beads to investigate the impact of coal fly ash pulverization on the generation rate and crystallinity of the synthesized zeolite. It was reported that the pulverization increased the phillipsite (a form of

zeolite) crystallinity. In another study, Inada et al. (2005) investigated the effect of MW radiation on the zeolite synthesis to examine the impact on yield during the reaction. Coal fly ash with a Si/Al ratio of 1:10 was added to 2M NaOH solution and then aged for 2h at 100°C using CH and MW methods. MW radiation in the first 15 min of the reaction period was observed as the best synthesis time that provided the highest cation exchange capacity of 2.00 meq/g.

However, to the best of our knowledge, there is no report in the literature on the efficiency of MW radiation for the synthesis of zeolites from WG cullet. Although MW hydrothermal synthesis of zeolites has been reported by many researchers, the mechanism of MW heating is not still fully understood and needs further exploration. In this study, we report a facile procedure to reuse beverage WG cullet separated from municipal solid waste, and produce value-added zeolites using a rapid MW synthesis technique. The detailed objectives of this study are as follows: i) to investigate the formation of zeolitic materials from beverage WG cullet via MW radiation and to compare the generated phases with materials synthesized through a CH method under the same starting conditions; and ii) to provide a comprehensive comparison between the performance of two different MW synthesis modes i.e. constant temperature and constant power in terms of nucleation, crystallization efficiency, and energy consumption. Although previous investigations have reported that aging prior to zeolite crystallization is an essential step for the nucleation of zeolite from intermediate gels (Jun et al., 2014; Baig et al., 2015; Polyzoidis et al., 2016; Bakare et al., 2015; Jury et al., 2014), satisfactory results obtained in the present work (without aging the samples) indicates that employing an aging period causes extra time, energy, and cost requirements that could be avoided to simplify the synthesis process.

3.2. Materials and methods

3.2.1. Materials

WG, in cullet form, was obtained from a local glass recycler, Cascades Recovery Inc. (Manitoba, Canada). First, the WG cullet was passed through a 30-mesh sieve (0.595 mm). To increase the surface-to-volume ratio of the sieved particles and produce very fine powders, the sieved WG cullet particles were ball-milled using a Laboratory Mill (MINICER from NETZSCH, Germany). Ten grams of the sieved WG were added to 200 mL of deionized (DI) water and milled in a rotating chamber containing 30 mm spherical ZrO_2 beads at a rate of 400 rpm for 40 min. The suspension, after ball milling, was kept overnight at room temperature to settle the glass phase, and the supernatant was then removed. The settled glass particles were oven-dried at 70°C for 24h, and the dried particles were then ground using a mortar and pestle to obtain a uniform and well-separated glass powder. Analytical grade sodium aluminate ($\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:3\text{H}_2\text{O}$; Sigma-Aldrich, USA) and sodium hydroxide (NaOH; Alphachem, Canada) were used as-received. DI water was used to provide a medium for the alkaline hydrothermal reaction.

3.2.2. CH and MW Zeolite Synthesis

The synthesis was done starting with amorphous aluminosilicate gel. For the CH technique, 1.80 g of the WG powder and 2.55 g of sodium aluminate were mixed well in 36 mL of 0.5 mol/L sodium hydroxide solution. The mixture was stirred for 20 min, poured into a 45 mL Teflon vessel and placed in an oven to be treated hydrothermally. The product was then filtered and washed three times with DI water. Samples were oven-dried at 70°C for 24h and ground with mortar and pestle prior to further characterization.

For MW synthesis, 1.41 g of sodium aluminate was added to 1 g of WG powder. In addition, 20 mL of 0.5 mol/L sodium hydroxide aqueous solution was prepared by adding 0.4g of NaOH pellets

to 20 mL of DI water. The solution was transferred into a 25 mL sealed borosilicate glass reaction vessel and stirred for 20 min. Next, the reaction mixture was exposed to radiation for hydrothermal treatment. The products were filtered, washed thrice with the DI water, and then oven-dried at 70°C overnight under the same conditions as the CH synthesis.

Several previous studies have identified the impact of acid pre-treatment of WG powder prior to the main alkaline hydrothermal reaction for the removal of impurities and synthesis of single-phase zeolites (Kim et al., 2015a; Tsujiguchi et al., 2014a; Kim et al., 2015b; Tsujiguchi et al., 2014b). However, in order to simplify the process and reduce cost, zeolite synthesis without acid pre-treatment was explored in the present work. It should be noted that for most applications, a mixture of zeolitic phases would serve the purpose, so that the synthesis of a single-phase zeolite may not be of paramount concern (Kuwahara et al., 2008, Cardoso et al., 2015).

MW synthesis experiments were conducted with two modes: i) MW constant temperature mode (MWCT), and ii) MW constant power mode (MWCP) that occurred in an MW chamber for varying times and temperatures. In the former, the temperature was kept constant with the adjustment of MW irradiation power; while, in the latter, the synthesis was performed at constant power. The radiation time was between 10 and 30 min for both modes. The temperature ranged between 80 and 150 °C in the MWCT mode, and the power was 50, 70, and 100 W in the MWCP mode. The synthesis was done in a self-adjusting single-mode microwave oven (2.45 GHz, CEM corporation, Discover, USA), where the power and temperature were automatically monitored. The synthesis temperature was monitored using an infrared pyrometer installed in the MW cavity. The system contains an MW generator, a heating chamber (cavity), and a laptop to record the temperature, pressure, and power profiles. All CH synthesis experiments were performed in the temperature range between 90 and 150 °C for 24 and 72 h utilizing a conventional oven (Fisher Scientific 516G,

USA), which followed the method described by the International Zeolite Association (IZA) (Robson, 2001).

3.2.3. Characterization

The synthesized materials were characterized using various analytical techniques. X-ray diffraction patterns were collected under ambient conditions with samples on a zero-background quartz slide, using a Bruker D8 DISCOVER with DaVinci with CuK_α (average $\lambda = 1.5418 \text{ \AA}$) over the range of $10^\circ < 2\theta < 90^\circ$. Phase matching analysis for the CH, MWCT, and MWCP products was done using DIFFRAC.SUITE EVA software and the best options offered by the phase matching software were selected. The results were corroborated with literature and reference patterns available in the crystallographic databases (Bukhari et al., 2014; Terzano et al., 2015; Gordon et al., 2012). The relative phase percentages (phase evolution) for each phase available in the synthesized products were obtained using EVA software based on the integrated area of each matched phase in a pattern. The crystallite size of the samples was calculated according to Scherrer's equation (Shoumkova and Stoyanova, 2013a).

The composition analysis for the WG cullet and synthesized zeolites were conducted using a energy dispersive X-ray spectrometer (EDX) (Hitachi, JSM-6701F, Japan). The Fourier transform infrared (FTIR) spectra of the samples were recorded using a Spectrometer (Perkin Elmer Spectrum, GX FTIR, USA) with a scan range of $400\text{-}4000 \text{ cm}^{-1}$ by pelleting the sample powder with KBr. Thermogravimetric (TGA) measurements were done using a Perkin Elmer TGA-7, USA. The samples were heated in the range of 20°C to 400°C at a heating rate of $1^\circ\text{C}/\text{min}$ under argon gas.

3.3. Results

3.3.1. X-ray Diffraction (XRD) Results

Figure 3-1 presents the XRD patterns of the synthesized zeolitic materials using the CH technique. According to the pattern matching results, in the CH-90°C-72h product, the major phases available were zeolite A ($\text{NaAlSiO}_4 \cdot 2.25\text{H}_2\text{O}$, JCPDS card no. 39-0222) with a mixture of NaP1 ($\text{Na}_{3.6}\text{Al}_{3.6}\text{Si}_{12.4}\text{O}_{32} \cdot 14\text{H}_2\text{O}$, JCPDS card no. 39-0219) and hydroxysodalite (HS) ($\text{Na}_6(\text{AlSiO}_4)_6 \cdot 6.4\text{H}_2\text{O}$, JCPDS card no. 42-0216) (Nchare et al., 2016; Degennaro and Colella, 1991; Khosravi et al., 2016; Xie et al., 2012; Fernández-Jiménez et al., 2008). In CH-90°C-24h, the same phases were produced; however, the broad hump at low angles increased compared to the former product due to the reduced reaction time indicates that the precursor amorphous glass was still present. The same phases were also observed for the CH-110°C-24h sample.

As the reaction temperature was increased to 120°C, the characteristic reflections corresponding to zeolite A (at the 2θ of 10.25°, 12.55°, and 16.20°) disappeared, and a two-phase mixture of NaP1 and HS resulted. Increasing the temperature from 120 to 130°C decreased the yield of zeolite NaP1 and HS and introduced a new phase of analcite ($\text{Na}(\text{AlSi}_2\text{O}_6) \cdot \text{H}_2\text{O}$, JCPDS card no. 41-1478) (Bejar et al., 2014). Further increasing the temperature to 150°C decreased the relative amounts of zeolite NaP1 and HS while the amount of analcite increased. In addition, we can see that as the temperature increased to 150°C the amorphous content decreased. This indicates less amorphous residual glass particles remained after synthesis at the higher temperatures.

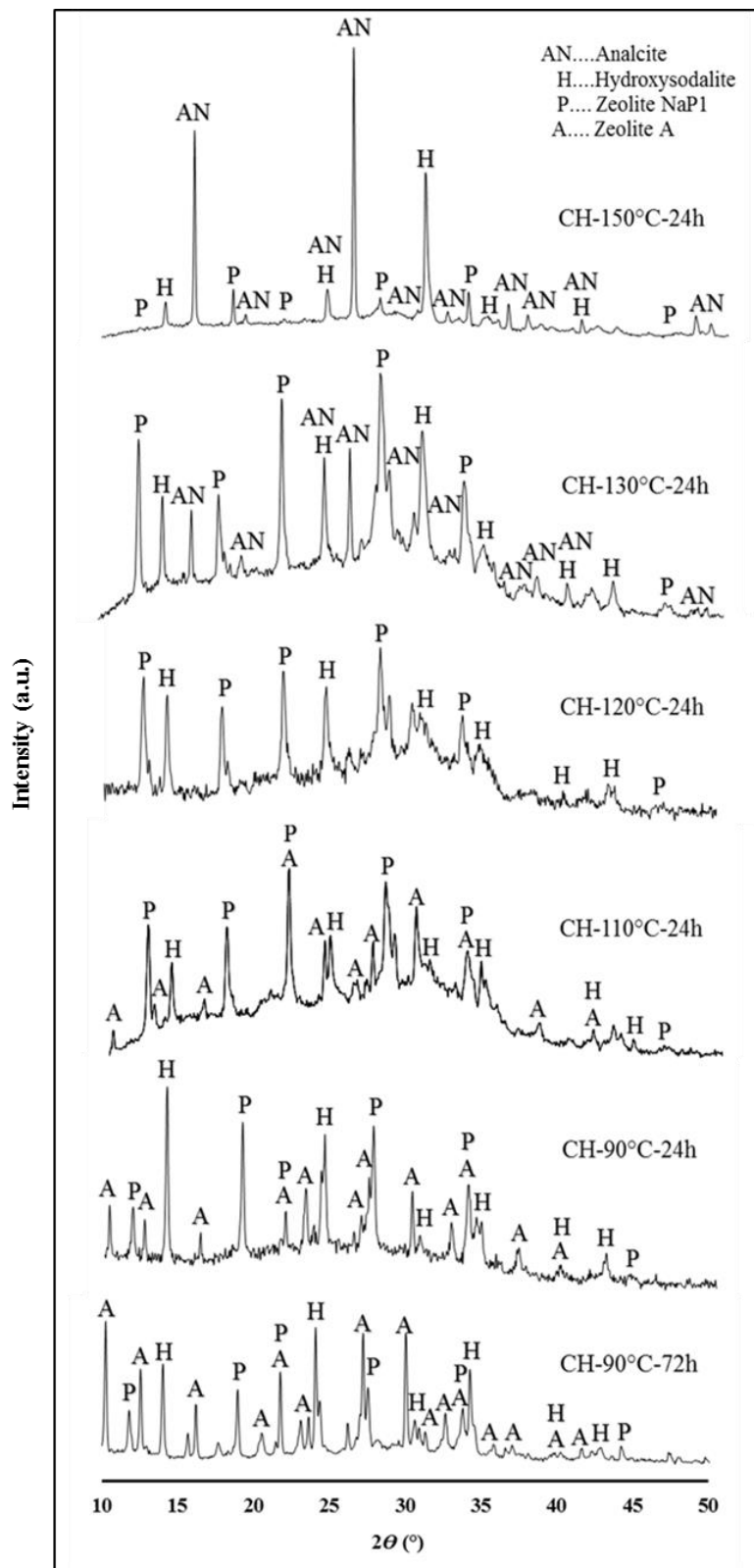


Figure 3-1. XRD patterns of the synthesized zeolites using CH method

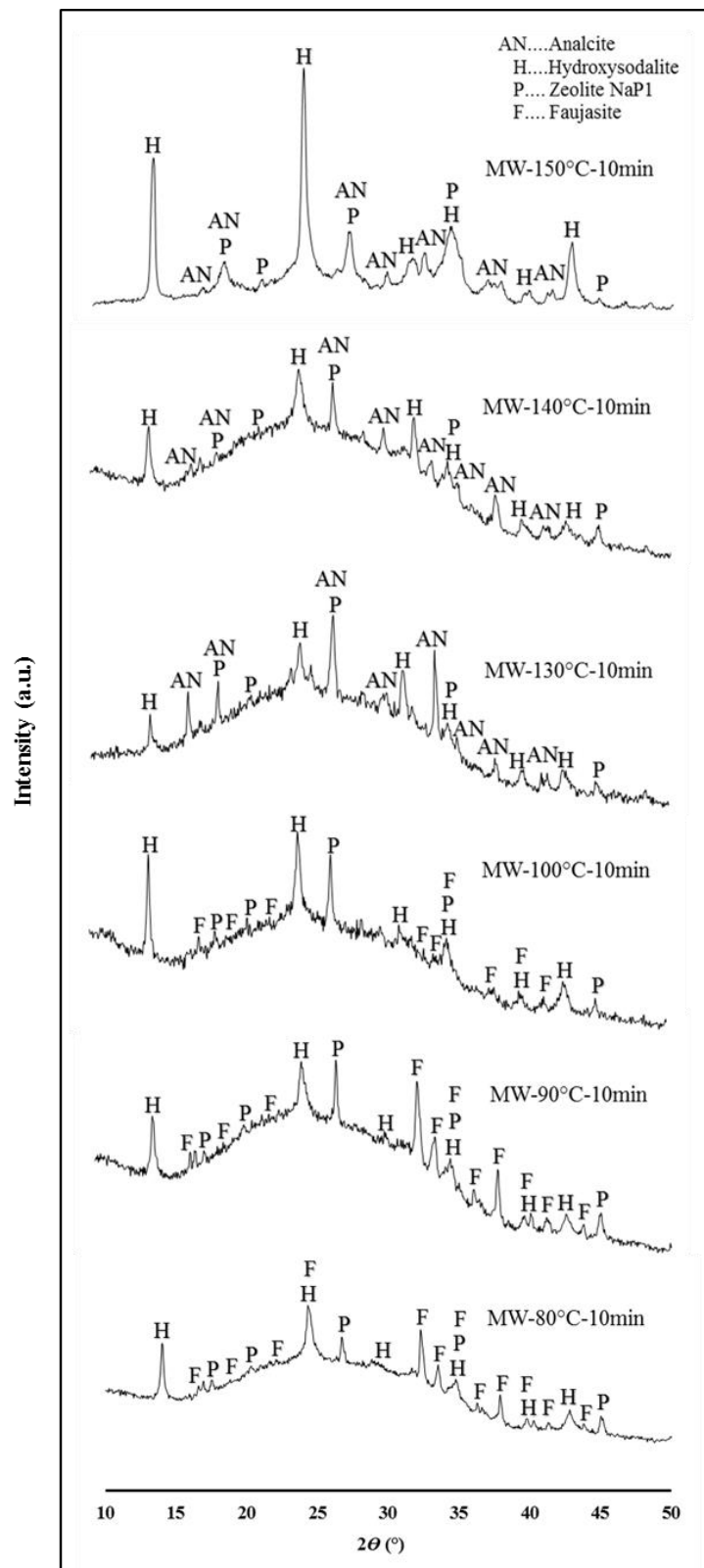


Figure 3-2. XRD patterns of the synthesized zeolites using MWCT mode

Figure 3-2 shows the XRD patterns of the synthesized zeolitic materials using the MWCT mode. Using the MWCT mode, lower temperatures (80-100°C) produced three-phase zeolitic materials that are a mixture of NaP1, HS, and Faujasite ($\text{Na}_2\text{Al}_2\text{Si}_{2.4}\text{O}_{8.8}\cdot 6.7\text{H}_2\text{O}$, JCPDS card no. 12-0246) (Zhang et al., 2014). As the reaction temperature was increased to 130°C, the reflections corresponding to Faujasite phase began to disappear and the characteristic reflections related to a new analcite phase appear. With a further increase in temperature from 130 to 150°C, the materials were still a mixture of the three zeolites NaP1, HS, and analcite. At 150°C, the intensity of the characteristic peaks associated with HS increased significantly; it is the main crystalline phase that results from this reaction temperature. The average crystallite size for the zeolites synthesized using CH and MWCT mode was approximately 35 and 23nm, respectively based on Scherrer analysis. The main reason for the larger crystallite size in CH zeolite compared to the MWCT zeolite could be due to the Ostwald ripening phenomenon occurring as a result of much higher crystallization time in CH. In fact due to this phenomenon, small crystals dissolve in the solution and deposit on the larger particles. Therefore, higher crystallization time would provide larger particles (Bukhari et al., 2015a).

The XRD patterns of the materials synthesized using the MWCP mode are exhibited in Figure 3-3. The types of zeolite phases synthesized were similar to those synthesized using MWCT mode (Faujasite, NaP1, and HS). This confirms that the heat generation mechanism, the gel dissolution procedure, and nucleation follow a similar evolution in constant power and constant temperature modes. Power increases did not influence the major phases synthesized under MWCP mode. All the patterns obtained for the MWCP mode (Figure 3) with different irradiation times from 10 to 30 min include a broad hump indicating the presence of a large amorphous SiO_2 -based phase fraction.

3.3.2. Phase Evolution Results

Figure 3-4 presents the relative phase percentages as well as the phase evolution trends of the products synthesized using CH and MWCT modes as a function of temperature. Fig. 3-4(a) shows that the relative phase percentage of zeolite A decreased from 32% to 19% as the temperature increased from 90 to 110°C, while the relative phase percentage of zeolite NaP1 increased from 19% to 45%. At 120°C, the zeolite A phase disappeared completely and the relative phase percentage of zeolite NaP1 increased considerably to 59%. This indicates that the zeolite A is an intermediate phase that could be transformed into a more stable phase of zeolite NaP1 at higher temperatures (Król et al., 2014).

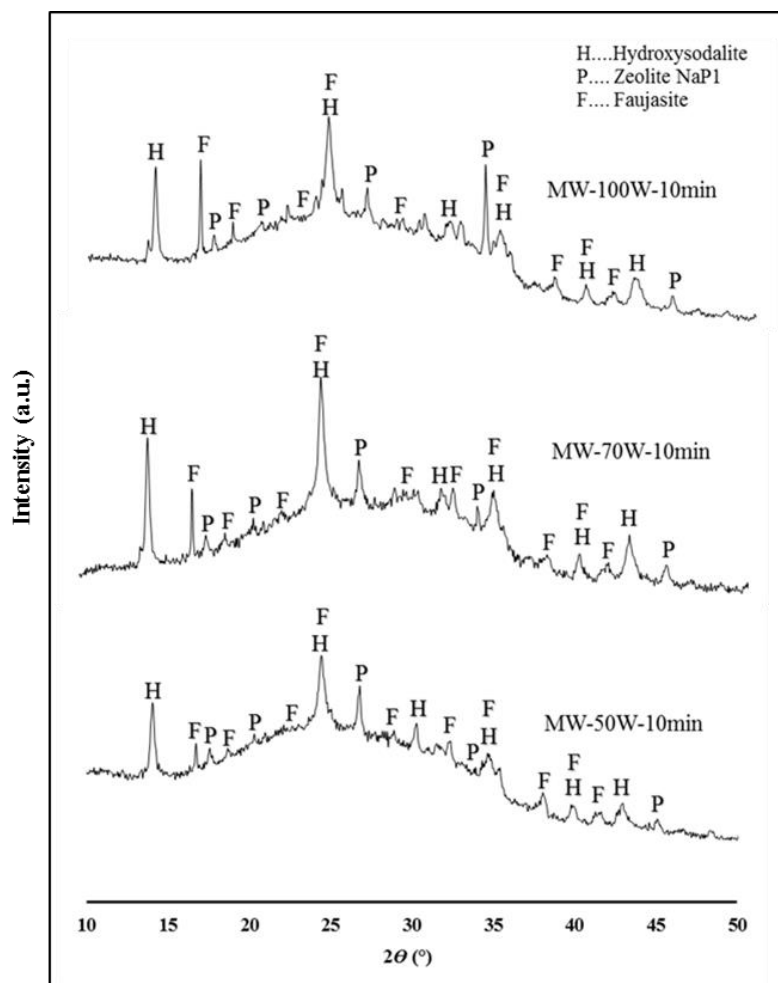


Figure 3-3. XRD patterns of the zeolites synthesized using MWCP mode

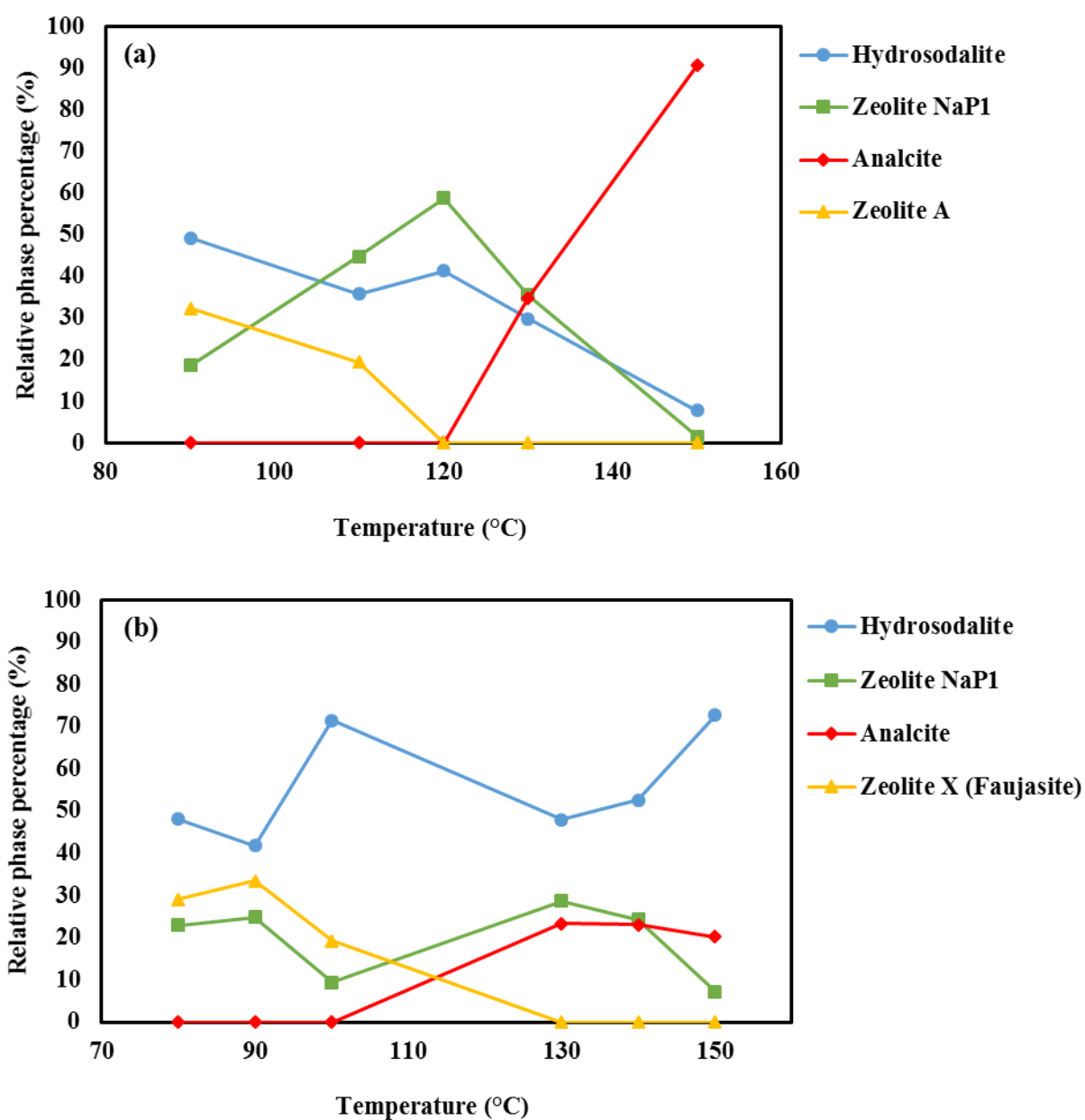


Figure 3-4. Phase evolution of the products synthesized under (a) CH at reaction time of 24h and (b) MWCT mode at 10min radiation time

With further temperature increase to 130°C, the relative phase percentages of zeolite NaP1 and HS decreased to 35% and 30%, respectively, as well as 35% for the new analcrite phase. This indicates that part of the zeolite NaP1 phase was transformed to the analcrite phase, as expected since at high

temperatures the zeolite NaP1 phase transforms into more stable phases such as analcite (Król et al., 2014). When the temperature increased to 150°C using CH, the phase percentage of the analcite phase reached a maximum of 91%.

The MWCT mode phase analysis shown in Figure 3-4(b) identifies that at lower temperatures (between 80 and 100°C), the phase fractions of zeolites NaP1 and Faujasite decreased and the corresponding fractions of HS increased. When the synthesis temperature was 130°C, the Faujasite phase fully disappeared, while the mixture of zeolites NaP1 and HS kept developing and analcite emerged as a new phase. This also identifies Faujasite as an intermediate phase and its transformation to more stable phases such as analcite and HS. At temperatures over 130°C, the HS phase fraction followed an increasing trend up to the maximum value of 73%. The results presented in Figure 4(b) show that HS using the MWCT mode is the main crystalline phase over the entire synthesis temperature range.

From Figures 3-4(a) and (b), we see that the HS phase evolution presented an opposite overall trend between CH and MWCT modes. In CH (Figure 3-4 (a)), HS followed an overall decreasing trend indicating that the HS crystallization reduced as the temperature increased to 150°C; while, analcite crystallization gradually increased and became the dominant phase with the further increase in synthesis temperature. However, using the MWCT method (Figure 3-4(b)) shows that the HS phase evolution had an overall increasing trend indicating that the MW radiation and dielectric heating (discussed above) favored the nucleation and crystallization of HS, particularly at high temperatures.

3.3.3. Energy Consumption Results

The amount of energy used during the MWCT and MWCP modes irradiation was calculated from the area under the power curves, depicted in Figure 3-5. It was observed in both modes that the

transferred energy in the synthesis process followed an increasing trend as the temperature, radiation power, and radiation time increased. The average amount of transferred energy during synthesis in MWCP mode varied from 75 to 257.14 KJ/g, which was much higher compared to

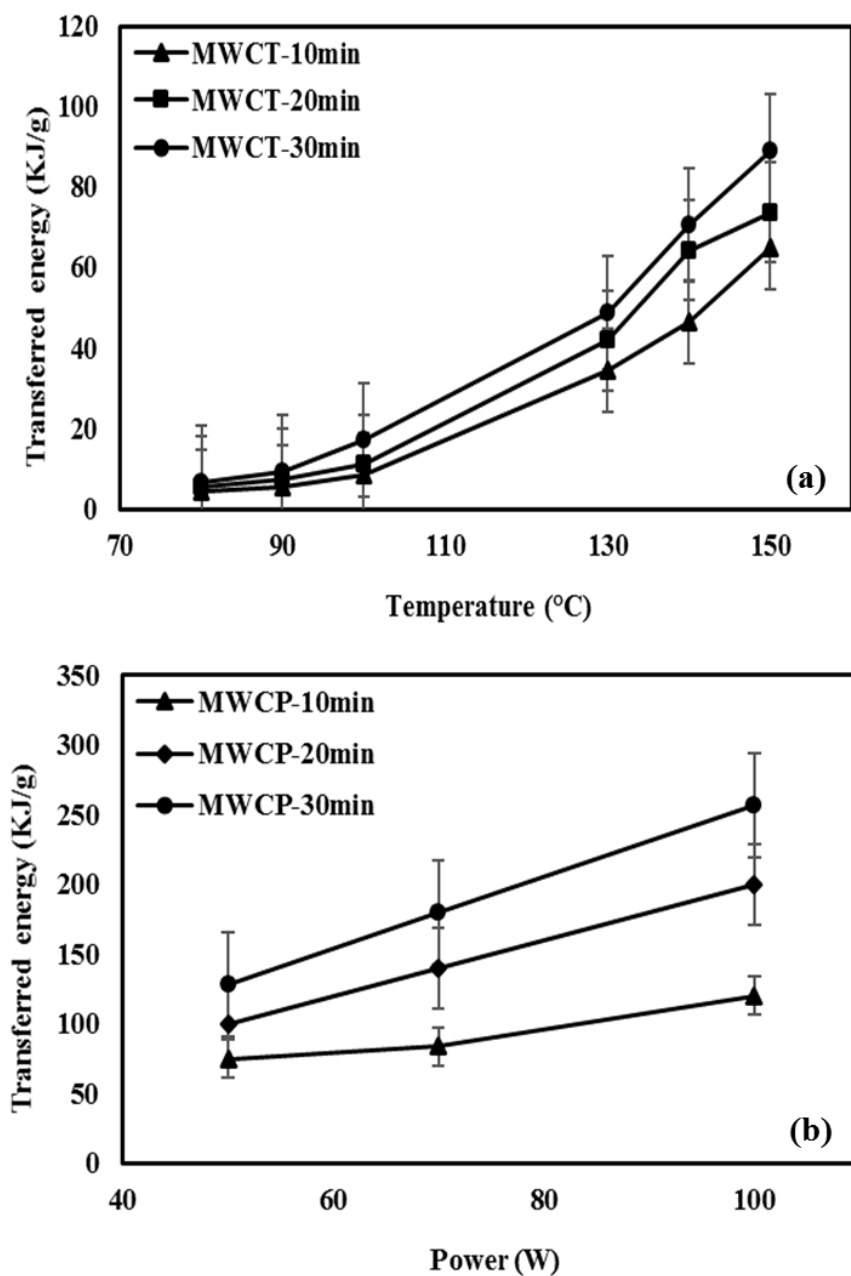


Figure 3-5. Transferred energy irradiated to the samples synthesized using (a) MWCT and (b) MWCP modes at different radiation times

the MWCT mode range of 4.25 to 88.94 KJ/g for the radiation time of 10 to 30 min. The energy transferred to the solution via MW radiation in MW-100W-30min was roughly 3 times higher than the energy transferred in MW-150°C-30min, shown in Figure 3-5.

3.3.4. Relative Crystallinity (RC) Results

The relative crystallinity (RC) of the synthesized zeolites using CH, MWCT, and MWCP modes is shown in Figure 3-6. The relative amorphous phase percentage was obtained by calculating the ratio of the area from the broadened reflections of the zeolitic materials synthesized through CH, MWCT, and MWCP modes to that of the broadened reflections identified in the pattern of the most amorphous sample (starting WG cullet powder, shown in Figure 3-7). The RC of the products was then calculated from the relative amorphous phase percentages. As shown in Figure 3-6(a), for both CH and MWCT methods the RC of the materials enhanced as the reaction temperature increased. The RC of both CH and MWCT materials reached a maximum of approximately 60% at 150°C. The RC results also demonstrate that 150°C is a critical temperature for producing zeolitic materials in a sealed vessel with the highest crystal growth efficiency for both CH and MWCT techniques, in agreement with the phase analysis discussed above. At 150°C, the MWCT mode with 10 min synthesis resulted in a zeolitic material with a similar RC (roughly 60%) as that of the zeolites synthesized using CH with 24h synthesis. MW synthesis requires approximately 1/144 the time of the CH method to yield the same zeolites – synthesis using MW irradiation offers an advantage of accelerating the zeolitization process from several hours to minutes.

Figure 3-6(b) presents the RC of the products synthesized using the MWCP mode for different radiation synthesis times. The overall RC for the products synthesized using a constant power mode (with a maximum RC of 19% at 50 W for 10 min radiation) was less than that of the products synthesized using the MWCT mode, particularly for the higher temperatures.

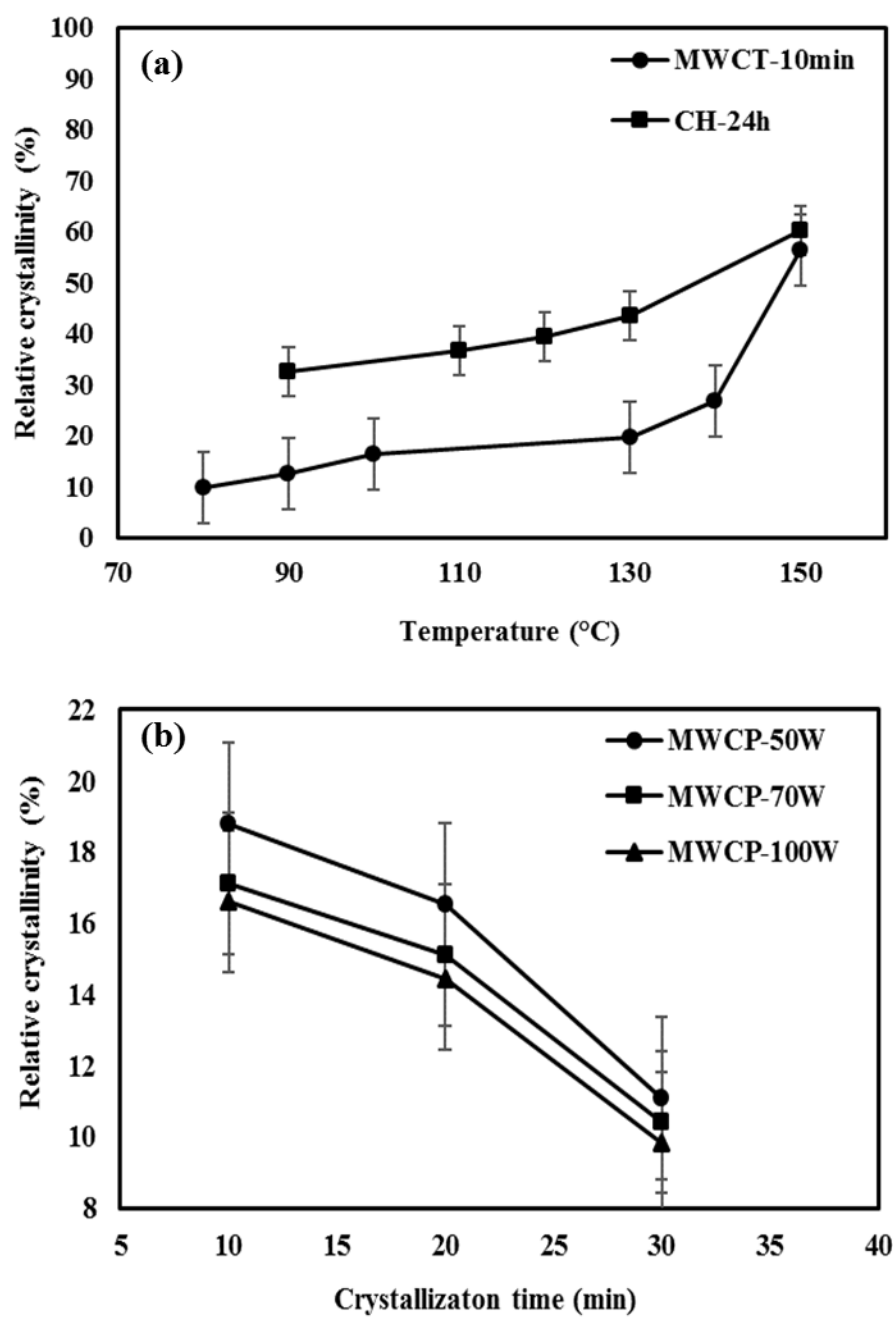


Figure 3-6. Relative crystallinity (RC) of the materials synthesized under (a) CH and MWCT as a function of temperature at 24h and 10min reaction and radiation time, and (b) MWCP products as a function of crystallization time

3.3.5. Energy Dispersive X-ray Spectroscopy (EDX) Results

Figure 3-8 shows the EDX analytical composition results of the WG cullet precursor and the zeolitic material of MW-150°C-30min. Si, Ca, Al, O, and Na were in the synthesized zeolites and

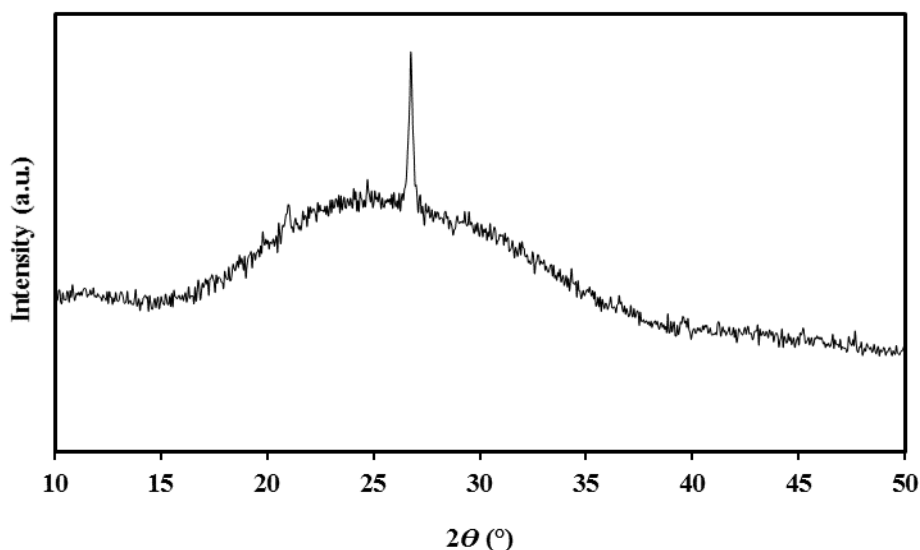


Figure 3-7. XRD pattern of the WG cullet powder

the WG cullet powder. The unlabeled peaks in Figure 3-8(a) correspond to C, Au, and Pt that originated from the Au coating evaporated onto the powder sample to reduce charging effects and the platform of the sample holder. The Na, Al, and Si peaks in Figure 3-8(b) correspond to the zeolitic product synthesized after alkaline hydrothermal treatment.

The decrease in the intensity of the Si peak in the zeolite sample indicates that not all Si content present in the WG cullet was utilized in the intermediate gel formation. Some of the Si-based content in the WG cullet is expected to be in the supernatant, which was discarded after the synthesis. On the other hand, the intensity of the peaks corresponding to Al and O increased after the zeolitization of the glass powder. This can be attributed to the addition of the sodium aluminate as the aluminum source and sodium hydroxide as the mineralizing agent to the solution at the initial stage of the reactions.

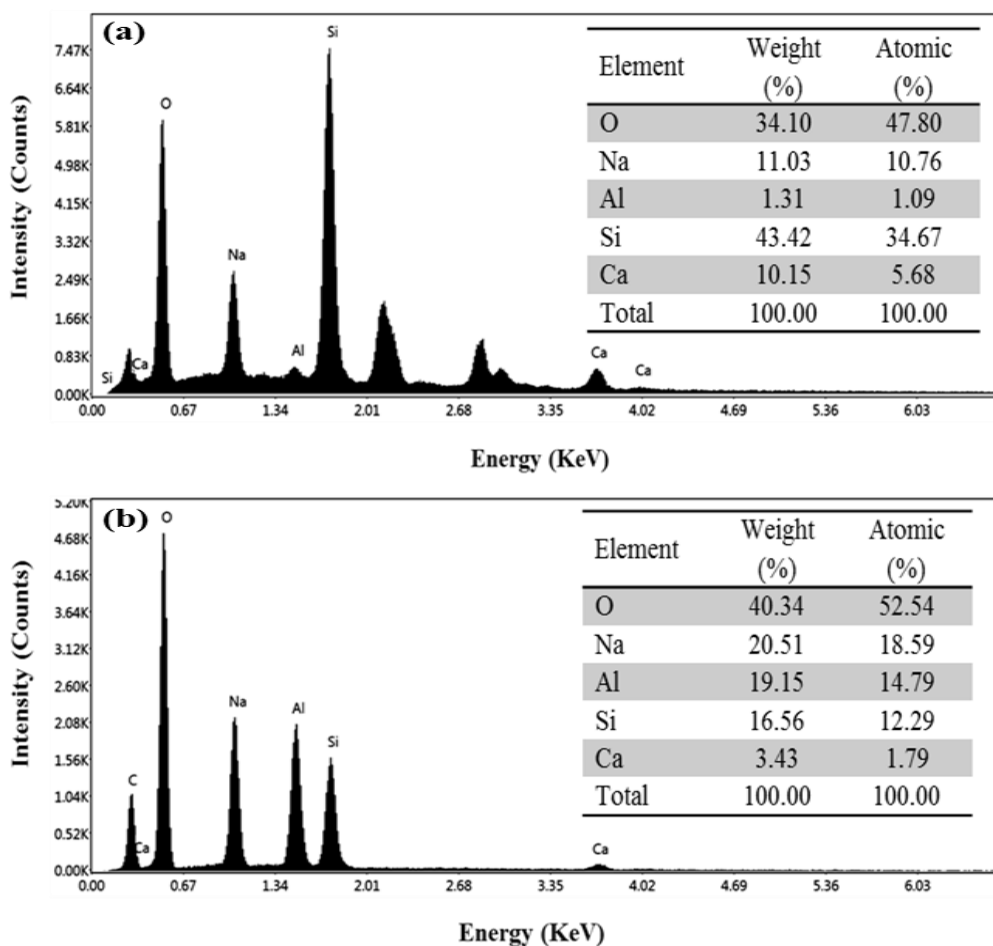


Figure 3-8. The EDX analysis of elemental composition for (a) WG cullet powder, and (b) MW-150°C-30min zeolite

3.3.6. Scanning Electron Microscope (SEM) Results

Figure 3-9 illustrates the SEM images taken for the WG cullet before ball milling, the glass powder after ball milling, and zeolitic materials synthesized through CH and MWCT mode to compare the growth of zeolite crystals. The morphologies represented by the SEM images for the samples synthesized under CH and MWCT mode confirmed the results observed through the XRD. Figure

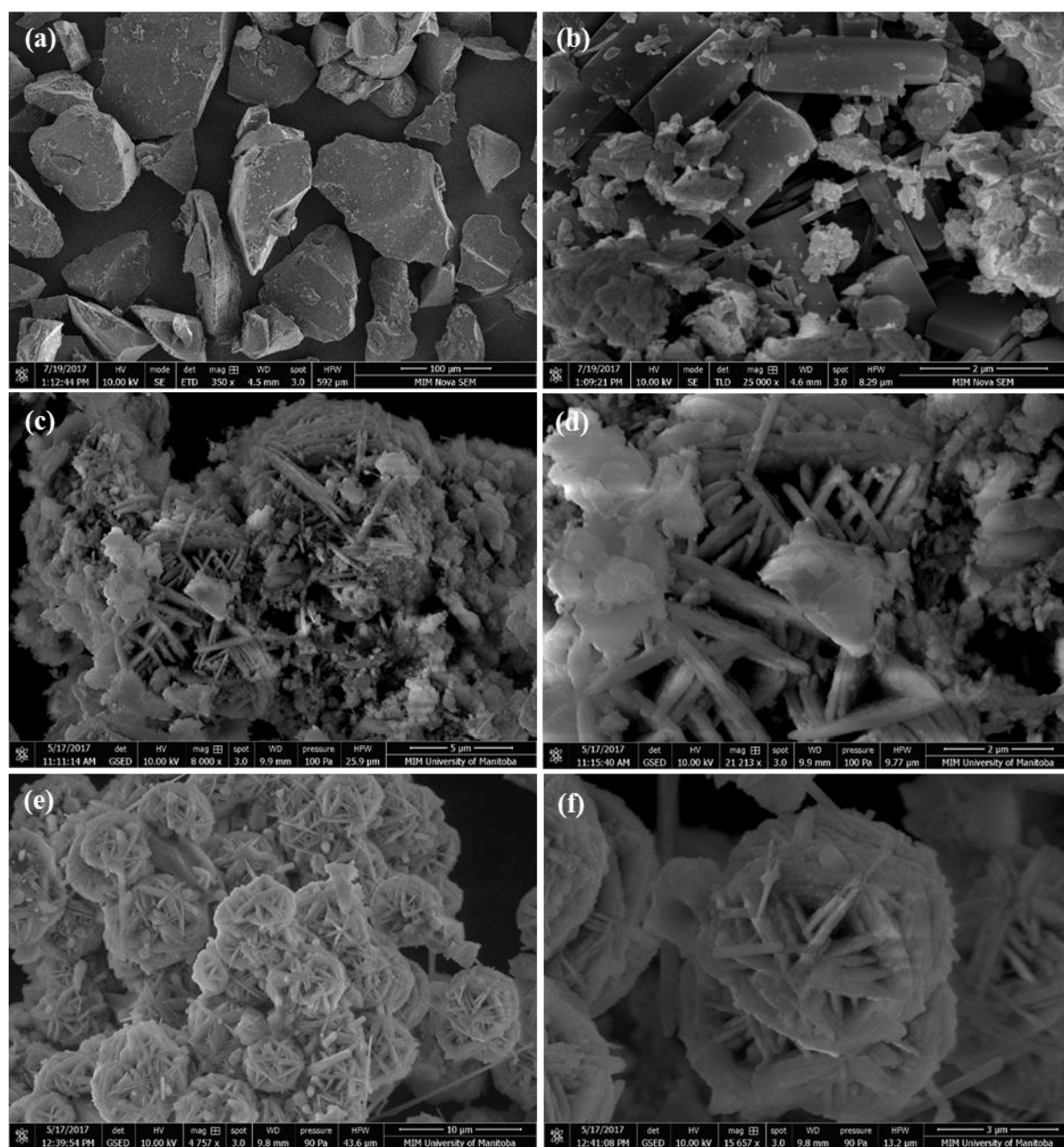


Figure 3-9. SEM images of (a) WG cullet powder before the ball milling; (b) glass powder after the ball milling; (c) and (d) CH-120°C-24h; (e) and (f) MW-150°C-10min

3-9(c) and (d) show the aggregated needle-like and flower shape structures originated from the zeolite NaP1 and HS synthesized under CH method at 120°C, respectively. Fig. 3-9(e) and (f) also show the same morphologies in the MWCT mode for the zeolites NaP1 and HS as well as the small rounded-edge cubes corresponding to the analcite phase. According to Figure 3-9(c), (d),

(e), and (f), the morphologies corresponding to HS, NaP1, and analcite were observed on the surface of the glass particles. Therefore, the crystals were nucleated and grew on the surface of the amorphous gel deposited on the surface of glass particles. This concurs with the literature that zeolite crystals are formed through a heterogeneous crystallization (Terzano et al., 2015; Inada et al., 2005).

3.3.7. Fourier-Transform Infrared Spectroscopy (FTIR) Results

FTIR is a very useful technique for obtaining vibrational information about the types of bonds present in materials. Therefore, some of the zeolitic products synthesized through CH and MWCT mode were subjected to FTIR analysis and the results are shown in Figure 3-10. Several characteristic bands were observed. The peaks at 1022 cm^{-1} correspond to the internal vibration of (Si, Al)-O asymmetric stretching; those at 689 cm^{-1} correspond to the internal vibration of (Si, Al)-O symmetric stretching; peaks at 467 cm^{-1} correspond to the vibration of (Si, Al)-O bending (Bukhari et al., 2015b; Shoumkova and Stoyanova, 2013b). The band related to O-H also appeared at about 1653 cm^{-1} .

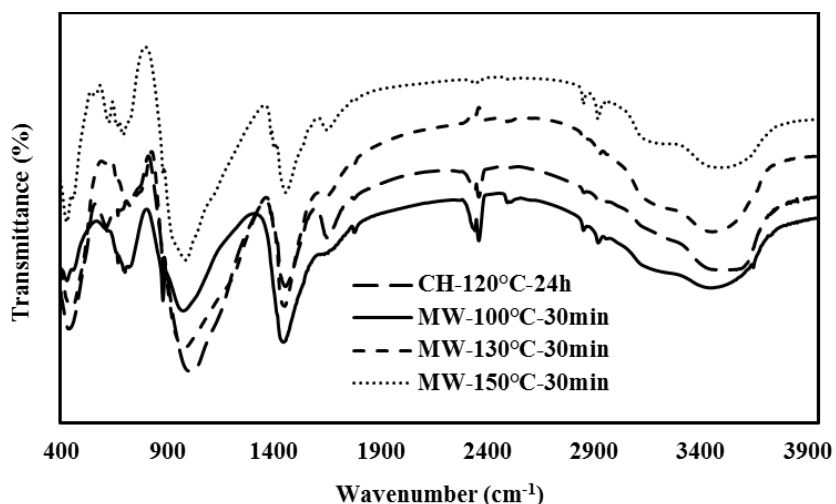


Figure 3-10. FTIR spectra of the zeolitic materials synthesized through the CH and MWCT modes

A broad characteristic peak is also observed at 3475 cm^{-1} , which is assigned to the vibration of the O-H stretching (Bukhari et al., 2015b; Shoumkova and Stoyanova, 2013b). These results are in agreement with the XRD phase identifications.

3.3.8. Thermogravimetry Analysis (TGA) Results

The ability of a zeolite to adsorb water into its framework is another important trait. TGA results of the WG cullet, as well as zeolitic materials synthesized using CH (24 hr) and MWCT (10 min) modes at $150\text{ }^{\circ}\text{C}$ are shown in Figure 3-11. The gentle slope correspond to the weight variations as well as the overall trend in the heat flow changes are specific behaviors of the WG cullet, which are attributed to the reversible sorption of the atmospheric moisture on the external surface and macropores of the WG cullet.

TGA results of the WG cullet showed a very small weight loss ($<1\%$), which was much lower than that of the materials synthesized through CH and MWCT methods (at 150°C) with weight losses of 12% and 10% , respectively. This weight loss indicates that the amount of adsorbed water in the synthesized zeolites was considerably higher compared to the WG cullet, consistent with the impact of the microporous structure and accessible surface area of the synthesized zeolites. The low variation in weight loss in zeolites produced under CH and MWCT mode (12% for CH and 10% for the MWCT mode) point to the similar surface area for both samples. The maximum weight loss for the two zeolitic samples occurred at 62 and 115°C for the CH and MWCT products, respectively (Figure 3-11(b)). These two points of inflection can be attributed to the evaporation of the adsorbed water content in the capillary micropores of the synthesized zeolites (Bukhari et al., 2015b).

3.3.9. Trends of Temperature and Pressure

Figure 3-12 shows the trends for the maximum temperature and pressure detected in the reaction vessel during the synthesis in both MWCP and MWCT modes. The vapor pressure ranged between 19 to 90 PSI as the temperature increased from 80 to 150 °C during MWCT mode synthesis. However, the pressure range in the MWCP mode was between 110 and 175 PSI, and temperatures

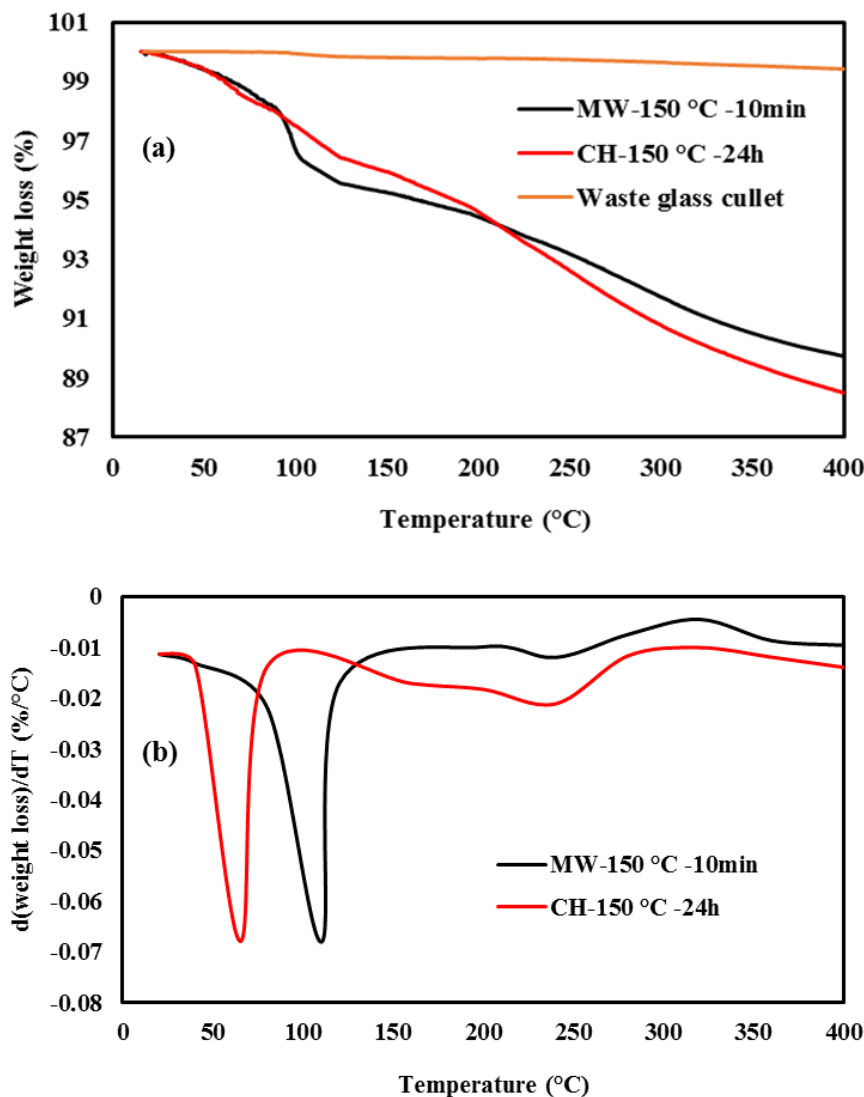


Figure 3-11. (a) TGA and (b) differential TGA scans of WG cullet, CH-150°C-24h and MW-150°C-10min

over 170 °C were measured during synthesis. These results indicate a temperature overshoot and high vapor pressure inside the vessel during synthesis in MWCP mode compared to MWCT. The variations of temperature and vapor pressure inside the reaction vessel are expected to influence zeolite formation.

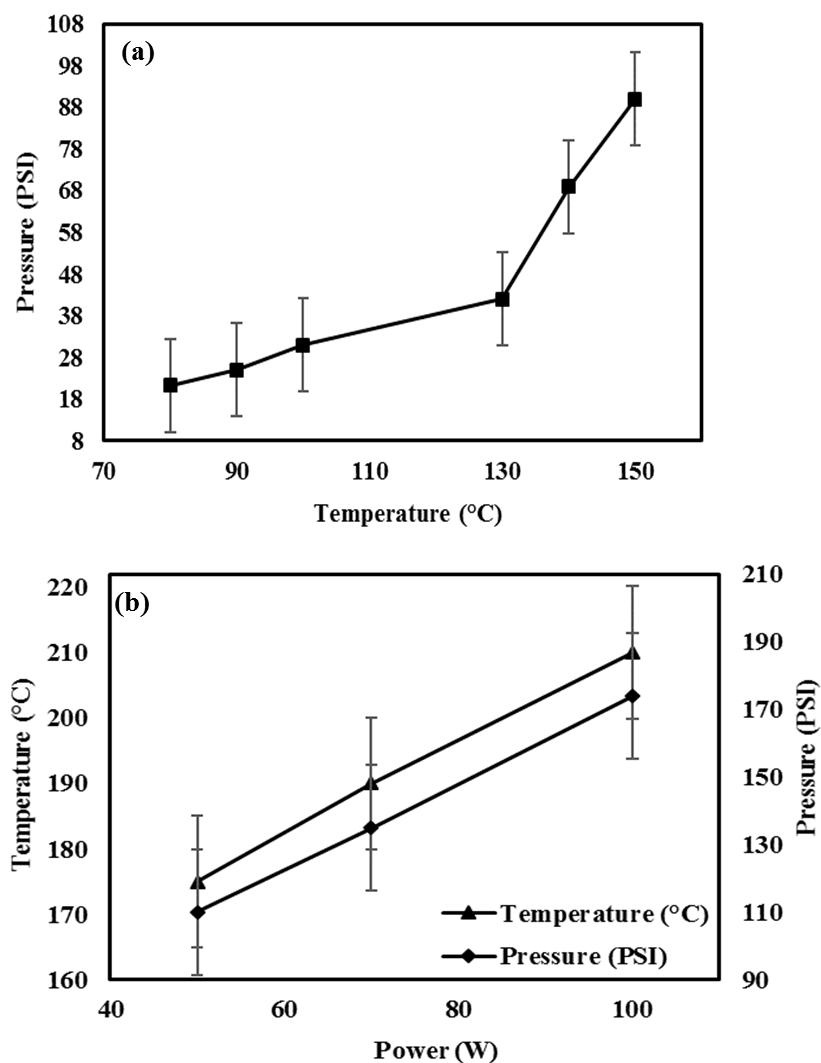


Figure 3-12. Maximum temperature and pressure detected during the synthesis in (a) MWCT and (b) MWCP modes

3.4. Discussion

3.4.1. Comparison of CH and MW Constant Temperature (MWCT) Results

Synthesis performed at MWCT mode with variable MW irradiation power showed that at least 10 min of radiation was necessary for satisfactory crystal growth. In addition to irradiation time, the hydrothermal temperature is also a major factor in the production of zeolitic crystals. Higher temperatures for both CH and MWCT synthesis modes increased the relative intensity of the XRD reflections, indicating products with better crystallinity (Nchare et al., 2016; Degennaro and Colella, 1991). XRD patterns of the materials made with CH and MWCT methods showed that the main zeolitic phases developed in temperatures above 130°C were similar (NaP1, HS, and analcite) using both techniques. However, two main differences were observed between the materials synthesized by CH and MWCT techniques. Firstly, zeolite A and Faujasite were synthesized at temperatures below 130°C using CH technique and MWCT mode, respectively, while the zeolites NaP1 and HS were synthesized in both methods. Secondly, at 150°C, the predominant phase of the CH method was analcite whereas using the MWCT method HS was the predominant crystalline phase. The combination of phases produced using either method at 150°C were the same.

These differences can be attributed to the interaction of the MW with the gel components in MW heating while this interaction is not available in CH. This interaction generates hot spot zones within the gel, particularly in zones where ions are present (Hoogenboom and Schubert, 2007). Formation of hot spot zones may favor the nucleation of one phase (HS) over another phase (analcite) in MW heating. However, in CH, when the hot spot zones are not generated analcite nucleation was favored over HS at 150°C. This difference could also be the reason for the formation of a more stable phase (i.e. Faujasite) instead of zeolite A in MWCT at temperatures

below 130°C; while zeolite A formed in CH without the generation of hot spot zones at the same temperatures.

According to the XRD results of Figures 3-1 and 3-2, the patterns obtained for the 150°C reactions showed the least amorphicity, so this temperature was the most effective in terms of the synthesis of predominantly crystalline materials. In general, it can be concluded that temperatures above the normal boiling point of the solutions (superheating synthesis) are most appropriate for the synthesis of crystalline zeolites from the WG cullet in a sealed vessel. This could be attributed to the reduction of strong hydrogen-bonding networks in a superheated liquid. As the strong hydrogen-bonding networks break down during superheated synthesis, highly active water molecules start their free thermal motion and attack the precursor WG particles and more Si release occurs (Inada et al., 2005). Following that, more nuclei would be available to improve the crystal growth.

3.4.2. Comparison of MWCT and MW Constant Power (MWCP) Results

To better clarify the relative efficiencies between the MWCT and MWCP modes, it is worth mentioning the comparison between trends of irradiation power and temperature profiles versus reaction time during the crystallization periods for samples MW-150°C-30min and MW-70W-30min. It was observed that in the constant temperature mode, the power of irradiation rapidly increased to over 200 W during MW-150°C-30min synthesis necessary for the required kinetic energy for dielectric heating of the solution. This resulted in a rapid temperature increase to the desired value of 150 °C in less than 2 min. Subsequently, the power decreased and remained at 20±10 W for the remaining 28 min to keep the temperature at 150± 3°C and complete the synthesis procedure.

However, in the constant power mode (MW-70W-30min), the electromagnetic field radiated at the fixed power level of 70 W, resulting in an overshoot of temperature to ~190 °C, much higher than the temperature set point. According to the XRD results presented in Figures 3-2 and 3-3, the material synthesized with 70 W constant power mode has a large amorphous component, despite the temperature overshoot. By contrast, 150 °C constant temperature mode synthesis resulted in high degree of crystallinity. This demonstrates that the temperature overshoot did not improve the crystal growth and retarded the nucleation and crystallization efficiency. It can be deduced that the MWCP mode is more energy consuming and consequently costlier compared to the MWCT mode, while it is less efficient for the synthesis of zeolites from WG cullet in a sealed system.

Figure 3-6(b) shows that the power increase adversely effected the RC of the zeolitic materials. Increasing the radiation time also reduced the RC of the products synthesized using the MWCP mode. Although the energy of radiation is higher in the constant power mode and the interaction with the electromagnetic field is active for a longer time, our results indicate that MWCP mode synthesized zeolitic products with higher energy consumption and lower RC. This denotes that transferring higher amounts of energy using MWCP does not improve the nucleation and crystal growth, and it may have an adverse effect on the RC of the products.

3.4.3. Possible Reasons of MWCP Mode Inefficacy

Possible reasons corresponding to the inefficacy of the MWCP mode in improving the RC of the zeolites synthesized using the WG cullet are as follows:

Firstly, the WG cullet used as the main silicate source contains metals (confirmed by the EDX analysis in this study) that may release free cations inside the reaction mixture whose presence make the reaction mixture more ionic with a high electromagnetic field adsorption capacity. The interaction of the available ions and MW can be more intense in MWCP compared to MWCT due

to the higher field energy of the fixed power mode. A more intensive interaction can result in a temperature overshoot as well as higher vapor pressure within the vessel that adversely affects the crystal growth. Watanabe et al. (1993) and Rezaei et al. (2016) reported that high pressure in the high temperature environment causes the degradation of the zeolite structure. The same observations were made in this study. Figure 3-12 shows much higher temperature overshoot and vapor pressure generation inside the vessel during synthesis in the MWCP mode, compared to the MWCT one, may have inhibited the crystal growth.

A second probable reason for the adverse effects of MWCP mode on the RC, nucleation, and crystal growth of the materials is that longer activation times of the MW in constant power mode provides much more energy for the dipolar molecules to convert the MW into heat (Madhusoodana et al., 2006). Therefore, the water molecules inside the solvent have higher kinetic energies and are much more active in the MWCP mode synthesis compared to the MWCT mode. It is assumed that nucleation in this case may be prevented since the nuclei are very unstable, being “attacked” by highly active water molecules in the MWCP mode (Madhusoodana et al., 2006).

The relative inefficacy of the MWCP mode could be improved by restructuring the MW apparatus with a reflux condenser at atmospheric pressure and heating the reaction mixture with MW radiation in an open-mode condition as reported in a recent study by Bukhari et al. (2015b). Open-mode synthesis would provide an efficient monitoring to minimize the temperature overshoot and high vapor pressure generation in the MWCP mode (Bukhari et al., 2015b).

3.5. Conclusions

The present work investigated rapid synthesis of various types of zeolites from the beverage WG cullet retrieved from MSW using a single-mode MW method in a sealed vessel using MWCT and MWCP modes without aging the samples and compared to those synthesized via the CH method.

Results suggest that an aging time could be avoided. Our results also revealed that MW heating was an effective technique for rapid conversion of the WG cullet to zeolite. However, it was most effective under certain radiation conditions. MWCT was an efficacious mode in the rapid synthesis of zeolites of the same quality as CH from WG cullet in superheating conditions. This considerably shortened the crystallization time from several hours to minutes. MWCP mode results in poorly crystallized materials, additional costs in terms of energy, and needs further modification of the apparatus to increase the efficiency of synthesis. In order to synthesize zeolites from the abundant WG utilizing novel techniques such as MW energy, more research has to be conducted on a pilot and industrial scale.

Chapter 4. Microwave Synthesis of Zeolites from Waste Glass Cullet Using Indirect Fusion and Direct Hydrothermal Methods: A Comparative Study *

Type of experiment	Scientific contribution
Microwave heating synthesis	A.R. Majdinasab conducted all the synthesis experiments using microwave heating technique.
XRD	A.R. Majdinasab prepared the samples and did the data collection.
EDX	A.R. Majdinasab prepared the samples and A. Khan from the Manitoba Institute of Materials (MIM) did the data collection.
SEM	A.R. Majdinasab prepared the samples and A. Khan from the Manitoba Institute of Materials (MIM) did the data collection.
FTIR	A.R. Majdinasab prepared the samples and did the data collection.
TGA	A.R. Majdinasab prepared the samples and Y. Wroczynskyj from the Department of Physics and Astronomy did the data collection.
Cation exchange capacity (CEC)	A.R. Majdinasab prepared the samples and did the data collection.

*This chapter has been published as: Majdinasab, A. R., & Yuan, Q. (2019). Microwave synthesis of zeolites from waste glass cullet using indirect fusion and direct hydrothermal methods: A comparative study. *Ceramics International*, 45(2), 2400-2410.

This chapter was fulfilled with the main objectives including: a) investigation of adding a fusion pretreatment stage prior to the main crystallization stage and exploring its impact on the properties of the zeolitic phases such as crystallinity, cation exchange capacity, and water holding capacity with respect to the products synthesized with direct hydrothermal method; b) studying the effect of high temperature/pressure environment on nucleation and crystal growth efficiency of the products, while synthesis occurs through constant temperature and constant power radiation modes.

The results obtained in this chapter contributed to the main objectives as they showed that zeolites synthesized by fusion of waste glass cullet provided higher crystallinity, cation exchange and water holding capacities compared to the zeolites produced by means of direct hydrothermal method. This chapter further contributed to the main objectives as they confirmed that high temperature and pressure overshoot in the course of microwave radiation could prohibit nucleation and crystal growth and may deteriorate the conversion yield. This chapter also suggested the application of cooling air jet on the reaction vessel wall as a promising alternative for the monitoring of the temperature and pressure overshoot.

Abstract

The present work studied the conversion of waste glass (WG) cullet into zeolite using microwave (MW) radiation technique. The temperature and power of radiation were monitored through constant temperature (MWCT) and constant power (MWCP) modes. Indirect fusion synthesis (IFS) and direct hydrothermal synthesis (DHS) conversion methods were studied and the zeolites synthesized by these methods were compared in terms of their characteristics using various techniques including XRD, EDX, SEM, FTIR, TGA, and cation exchange capacity (CEC). IFS was an efficacious synthesis technique and produced zeolites with a much higher crystal growth efficiency compared with those synthesized by DHS method. The IFS method was better than the DHS method as it eliminated the inhibitive effect of soluble aluminates on Si release. The IFS zeolites also provided lower Si/Al ratio and consequently higher cation exchange and water holding capacities compared to DHS zeolites, as validated by EDX, TGA, and CEC results. In addition, high pressure and high-temperature environment deteriorated the zeolite structure and diminished the crystal growth performance. The application of cooling air jet (CAJ) through MWCP mode provided efficient monitoring of temperature overshoot and excessive pressure generation by cooling the excessive generated hot spot zones. Therefore, the CAJ application improved the crystal growth in IFS method as higher radiation powers were applied.

4.1. Introduction

Zeolites are microporous hydrated aluminosilicate materials that possess small regular internal cavities (<2 nm) with high thermal, mechanical, and chemical stability. Due to these properties, they are utilized for different industrial purposes such as water filtration, gas sorption, and soil remediation (Weckhuysen, 2015). Although traditional zeolite synthesis methods involve the utilization of pure chemicals, several other materials have been proposed as alternative precursors for zeolite synthesis using alkaline hydrothermal reactions. So far, other aluminosilicate-based materials including paper sludge ash, rice husks, and coal fly ash have been utilized for zeolite synthesis purposes (Shoumkova and Stoyanova, 2013a; Dey et al., 2012; Behin et al., 2014; Cardoso et al., 2015; Kuwahara et al., 2008).

Utilization of aluminosilicate-based waste residues as the preliminary precursors for zeolite production may elevate the associated risks, especially when incineration wastes such as fly ash are utilized. It is proposed that these residuals could contain toxic elements including Cd, Pb, Hg, Cr (VI), and As that may restrict the wide application of such materials to synthesize zeolites (Terzano et al., 2005). On the other hand, utilizing pure chemicals to synthesize zeolites could be cost-prohibitive, making the products economically unfeasible for agricultural and environmental applications. Therefore, new cost-effective approaches are desirable for the clean zeolite synthesis to meet the large-scale industry demands for such materials.

Waste glass (WG) cullet procured from beverage bottles is conveniently accessible through separate collection systems of domestic solid wastes, and is predominately free of the potential toxic elements. Nowadays, most processes used to recycle the collected WG comply with environmental and economic aspects, although these procedures necessitate the employment of extremely high temperatures (up to 1600°C) based on the glass composition (Blengini et al., 2012).

Accordingly, greenhouse gas generation and high-energy requirement are the main downsides of these recycling methods. The most appropriate solution to these problematic issues is to convert the WG cullet into high value-added materials like zeolite. Since WG cullet has a high proportion of SiO_2 , it is proposed as a suitable precursor for the zeolite synthesis.

The conversion of WG cullet to zeolite is a type of hydrothermal process involving dissolution, condensation, nucleation, and crystal growth occurring at medium to high temperatures provided by conventional heating techniques (Shoumkova and Stoyanova, 2013b; Kim et al., 2015a; Terzano et al., 2015). Recently, the application of novel alternative energy sources such as microwave (MW) and ultrasound to synthesize porous materials has blossomed due to the impact on nucleation and induction periods (Sabouni et al., 2010; Chindaprasirt et al., 2013; Bukhari et al., 2015a; Kim et al., 2015b).

It has been reported that MW radiation reduces the induction period and remarkably improves the nucleation bottleneck (Bukhari et al., 2015b). MW radiation offers several advantages over conventional heating techniques for the synthesis of zeolites including elimination of by-products, reduction of the crystallization period, providing narrower size distributions, producing various morphologies, and accelerating the nucleation period (Katsuki et al., 1999; Bonaccorsi and Proverbio, 2003; Madhusoodana et al., 2006). MW radiation could also provide the conditions for superheating synthesis by elevating the normal boiling point of the solution, if the vessel is being pressurized (Bukhari et al., 2015a).

So far, several procedures are stated in the literature for the conversion of several solid precursors like coal fly ash to zeolite. These methods include direct hydrothermal synthesis (DHS), two-step hydrothermal synthesis, molten salt liquid free synthesis, and indirect fusion synthesis (IFS) (LaRosa et al., 1992; Hollman et al., 1999; Park et al., 2000; Kazemian et al., 2010). Most

pioneering studies working on the DHS and IFS methods utilized coal fly ash as the starting precursor using conventional heating techniques. Molina and Poole (2004) investigated DHS and IFS methods by varying the reaction conditions such as time, temperature, and NaOH to coal fly ash ratio. They reported that the crystallinity and cation exchange capacity (CEC) of the IFS zeolites were considerably higher than that of DHS zeolite. In another study, Sakthivel et al. (2013) converted coal fly ash to zeolite as a possible measure to clean up oil spills. They reported that the IFS zeolite demonstrated higher capacity for oil adsorption compared to DHS one.

Therefore, zeolites have been readily synthesized from various waste precursors by conventional heating techniques using IFS method. However, there is no existing report in the literature regarding the MW synthesis of zeolites from WG cullet as the starting precursor using IFS method. Besides, there is no study that compares the DHS and IFS methods while using MW radiation at high pressures. This study uses novel energy alternative, i.e. MW radiation instead of conventional heating technique to accelerate the crystallization of WG cullet using IFS method. The primary objective of this study is to provide a comparison between DHS and IFS conversion methods utilizing MW radiation in terms of gel growth mechanism, nucleation, and degree of crystallinity. Secondly, a comprehensive comparison between the performance of two different MW synthesis modes, i.e., constant temperature (MWCT) and constant power (MWCP) modes using both DHS and IFS methods is provided. The effect of MW cooling air jet on the efficient monitoring of the temperature and pressure within the vessel in MWCP mode and crystal growth of the products is also studied.

4.2. Materials and methods

4.2.1. Materials

WG, in cullet form, was received from the Manitoba Liquor and Lotteries recycling plant (Manitoba, Canada). WG cullet was passed through a 30-mesh sieve (0.595 mm), which was subsequently ball-milled using a Laboratory Mill (MINICER NETZSCH, Germany) to promote the surface-to-volume ratio of the sieved particles and produce very fine powders. Ten grams of the sieved WG were added to 200 mL of deionized (DI) water and milled in a rotating cavity containing 30 mm spherical ZrO₂ beads at a rotating speed of 400 rpm for 40 min. Once ball milling done, the suspension was kept overnight at room temperature to settle the glass phase, and the supernatant was then discarded. The settled glass particles were oven-dried at 70°C for 24h, and the dried particles were then ground using a mortar and pestle to obtain a uniform and well-separated glass powder. Analytical grade sodium hydroxide (NaOH; Sigma-Aldrich, USA) and sodium aluminate (Na₂O:Al₂O₃:3H₂O; Sigma-Aldrich, USA) were utilized as-received. To provide a medium for the alkaline hydrothermal reaction DI water was used as the solvent.

4.2.2. DHS Conversion method

A single-step alkaline hydrothermal treatment was employed to convert WG cullet into zeolite using DHS method. In this case, zeolite synthesis process was carried out as follows:

1.41 g of sodium aluminate was initially added to 1 g of WG powder. In addition, 20 mL of 0.5 mol/L NaOH aqueous solution was prepared by adding 0.4 g NaOH granules to 20 mL of DI water (NaOH/WG ratio of 0.4). The mixture was conveyed into a 25 mL sealed borosilicate glass reaction vessel and stirred for 20 min at room temperature. Consequently, the reaction solution was exposed to MW radiation for hydrothermal treatment. The amorphous gel was crystallized using a self-adjusting MW apparatus (2.45 GHz, CEM corporation, Discover, USA). The apparatus automatically controlled the radiation power and temperature by MWCT and MWCP modes. In

the former, the temperature was retained constant with the accommodation of MW power of radiation; while, in the latter, the synthesis was conducted at fixed power. Zeolites were synthesized after MW radiation exposure time of 10 min for both modes. The temperature ranged between 80 and 150°C in the MWCT mode, and the power was stabilized at 50, 70, and 100 W in the MWCP mode. The temperature and pressure measurements were taken using an infrared pyrometer and a pressure sensor, respectively, which was installed in the MW cavity. The system contains an MW generator, a heating chamber (cavity), and a laptop to collect temperature, pressure, and power data. In the next step, the products were filtered, washed thrice with the DI water, and then dried at 70°C overnight in an electric oven.

4.2.3. Indirect Fusion Synthesis (IFS) Conversion method

The conversion of WG cullet into zeolite using IFS method requires the NaOH solid fusion with WG powder at elevated temperatures prior to the main alkaline hydrothermal reaction (Shigemoto et al., 1993). The IFS experiments were conducted in the following way.

0.4 g of NaOH pellets and 1 g of WG powder were fused at 550°C for 2h. Next, the fused solid was ground using mortar and pestle to provide a uniform and well-separated powder, and diluted with 20 mL of DI water. Then at room temperature, the reaction mixture was stirred for 2h. Next, 1.41 g of sodium aluminate was added to the solution and the mixture was stirred for 20 min at room temperature prior to the MW radiation. The following procedure was similar to the DHS conversion method. In this study, the MW cooling air jet was applied to the reaction vessel wall during the MWCP radiation mode in IFS method to effectively monitor the temperature and pressure within the vessel while it was not applied in DHS method. In the present work, DHS zeolites are regarded as control materials (C) and IFS zeolites are regarded as fused materials (F).

An overview of the IFS and DHS methods for synthesis of zeolites from WG cullet using MW radiation technique is illustrated in Figure 4-1.

4.2.4. Characterization

Various analytical techniques were used to characterize the synthesized materials. X-ray diffraction (XRD) data were collected under ambient conditions with samples on a zero-background quartz slide, using a D8 ADVANCE Bruker diffractometer with $\text{CuK}\alpha$ (average $\lambda = 1.5418 \text{ \AA}$) over the range of $10^\circ < 2\theta < 40^\circ$. All the samples were normalized as the slide contained

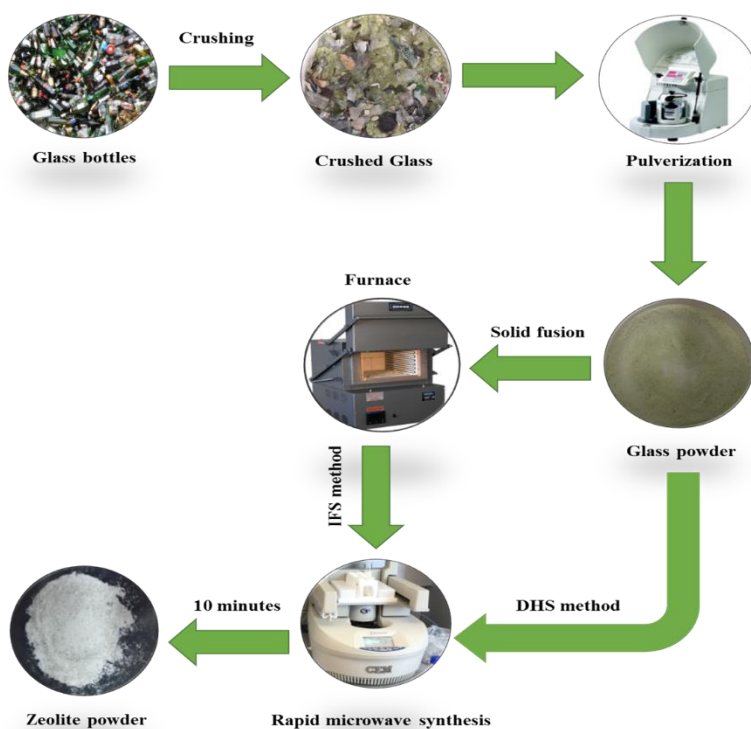


Figure 4-1. An overview of the DHS and IFS methods for zeolite synthesis from WG cullet using MW radiation

a 1-mm hole to adjust the zero background for all specimens. Phase matching analysis for all the products was done using DIFFRAC.SUITE EVA software and the best options offered by the phase matching software were selected. The results were corroborated with literature and reference

patterns available in the crystallographic databases (Tsujiguchi et al., 2014; Bukhari et al., 2014). The relative phase percentages (phase evolution) for each phase available in the synthesized products were obtained using EVA software based on the ratio of the crystalline peak area of each matched phase to the total peak area in a pattern. In this method, the characteristic line for each phase was first scaled to 100%, while other peaks were scaled relative to that value. The mentioned ratio was then calculated by the software.

Morphology of the crystals was studied using a Scanning electron microscope (SEM) (JSM-6701F, Hitachi, Japan) operated at 10 kV accelerating voltage. Composition analysis for the WG cullet, fused WG (FWG), and synthesized zeolites were conducted using an energy dispersive X-ray spectrometer (EDX) (JSM-6701F, Hitachi, Japan). The Fourier transform infrared (FTIR) spectra of the zeolites were recorded using a Spectrometer (GX FTIR, Perkin Elmer Spectrum, USA) with a scan range of 400-4000 cm^{-1} by pelleting the sample powder with KBr. Thermogravimetric (TGA) measurements were taken by a thermal analyser (TGA-7, Perkin Elmer, USA). The samples were heated in the range of 30°C to 500°C at 1°C/min rate using argon gas. The measurement of the samples Cation exchange capacity (CEC) was done using NH_4Cl saturation method proposed by Bain and Smith (1987). Briefly, 1 g of the sample was added to 50 mL of 1M NH_4Cl aqueous solution (pH 7, saturated with NH_4^+ ion). The mixture was stirred and allowed to reach the equilibrium. Next, the mixture was centrifuged and the supernatants of all samples were collected for further analyses. The collected supernatants were diluted twice to adjust the concentration within the detection limit of the apparatus. The ammonium ($\text{NH}_4^+\text{-N}$) concentration of the diluted samples was measured using a flow injection analyzer (FIA) (Quick Chem 8500, LACHAT Instruments, USA) with the detection limit of 0.2 mg/L.

4.3. Results

4.3.1. XRD Results

4.3.1.1. WG and FWG

Figure 4-2 depicts the XRD patterns of the WG cullet and FWG. It can be clearly seen that the amorphous content of the WG cullet decreased after fusion. The XRD pattern of the FWG shows some new peaks that are related to the soluble silicates originally available in WG cullet (Bukhari et al., 2014). The soluble silicates are generated due to NaOH incorporation into the amorphous phases of the WG framework at high temperatures, making it more convenient to dissolve in the solution compared to the amorphous and crystalline silicates available in unfused WG cullet (Bukhari et al., 201; Shigemoto et al., 1993). The incorporation of the solid NaOH into the WG framework via fusion not only has an efficient impact on WG dissolution, but also improves the conversion rate.

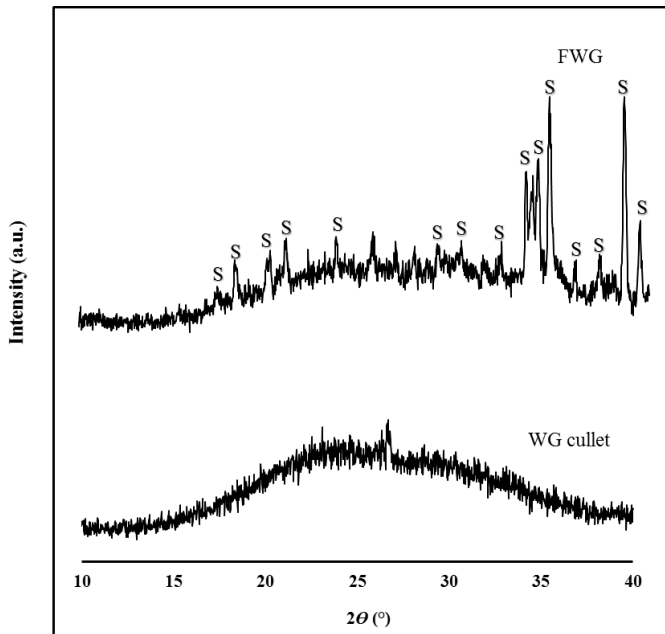


Figure 4-2. XRD patterns of the WG cullet and FWG (Characteristic peaks S represent soluble FWG)

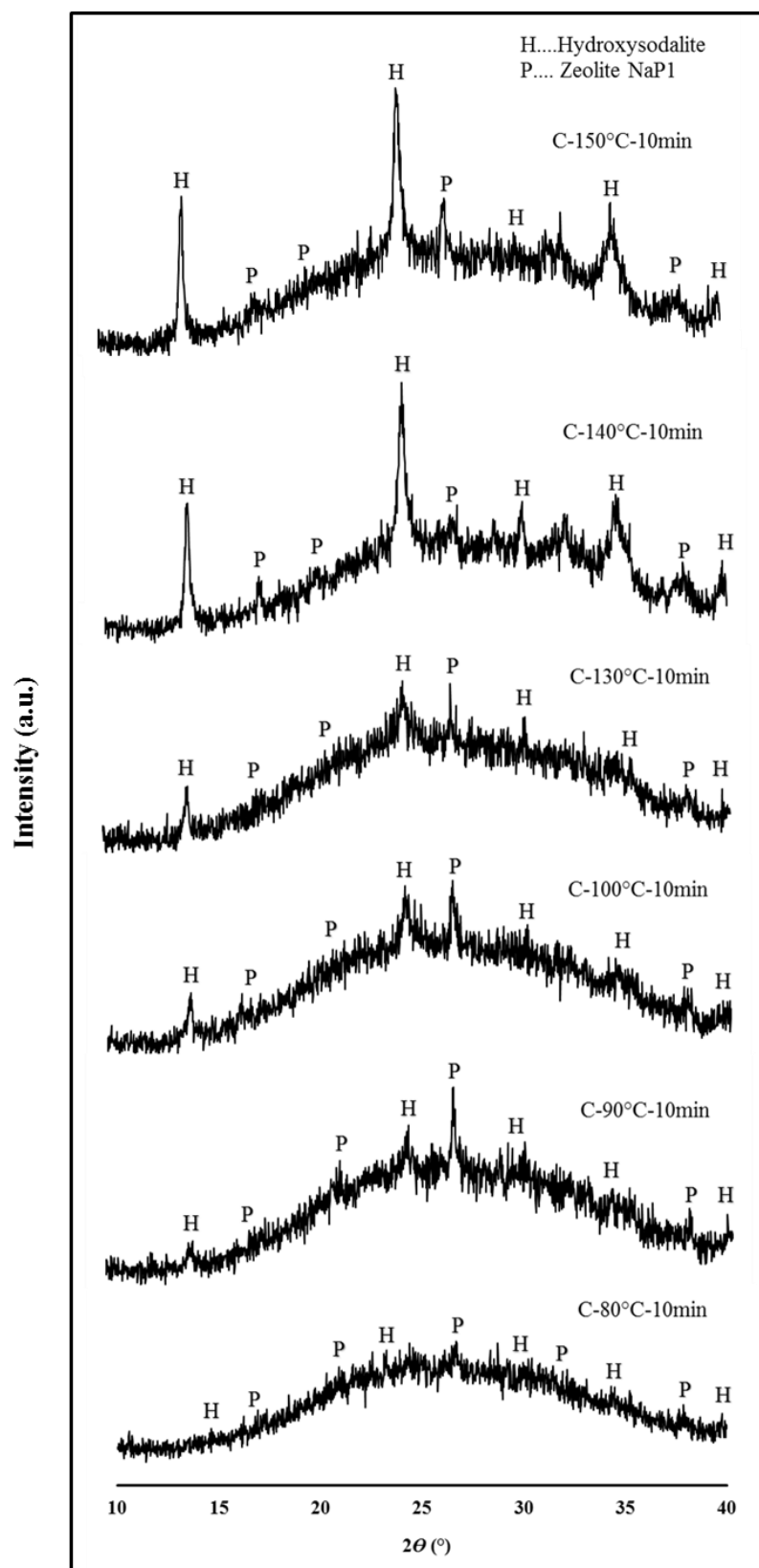


Figure 4-3. XRD patterns of the zeolites synthesized by DHS method via MWCT mode

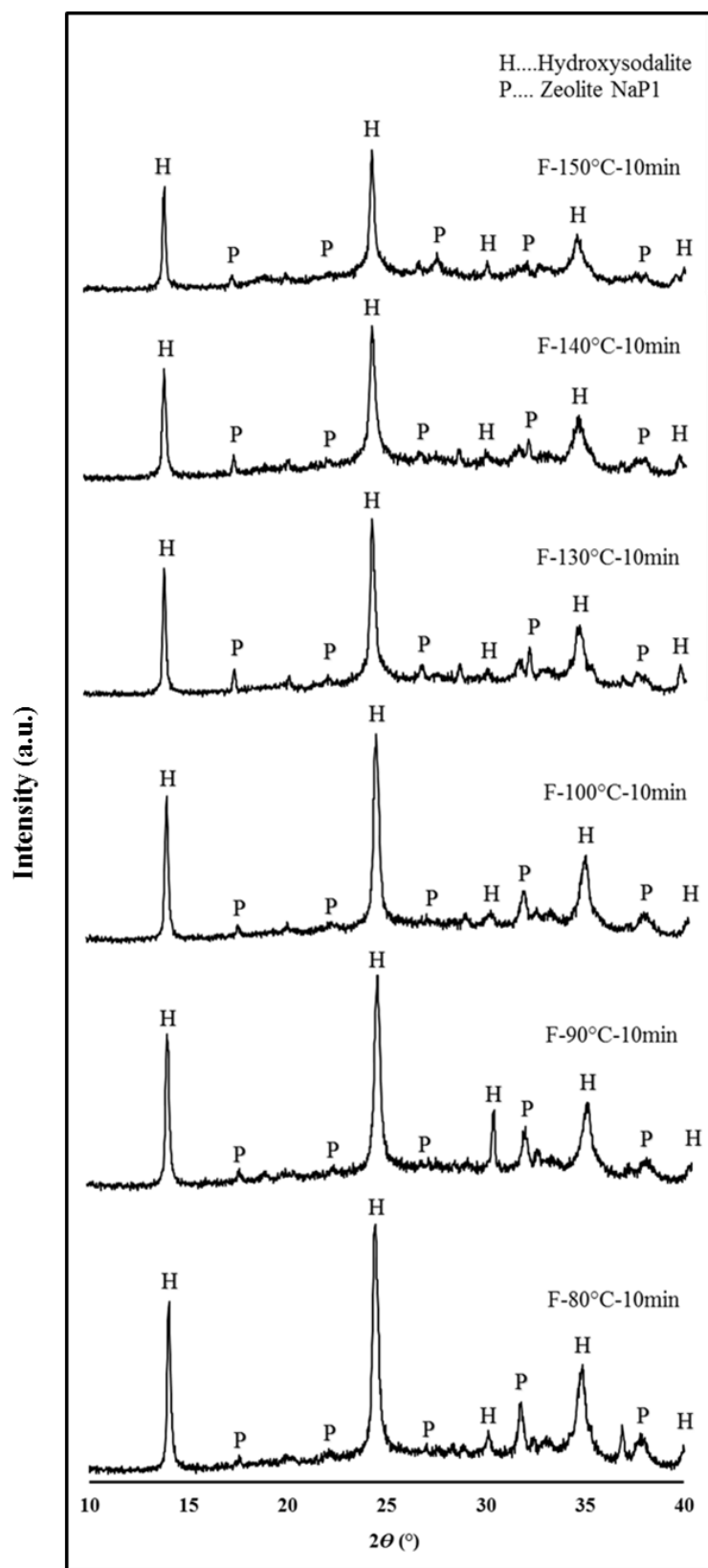


Figure 4-4. XRD patterns of the zeolites synthesized by IFS method via MWCT mode

4.3.1.2. Zeolite production via MWCT Mode

Figures 4-3 and 4-4 depict the XRD patterns of the zeolites synthesized by DHS and IFS methods via MWCT mode. The characteristic peaks observed at 2θ ranging from 10° to 40° matched with those for Hydroxysodalite (HS) ($\text{Na}_6(\text{AlSiO}_4)\cdot 6.4\text{H}_2\text{O}$, JCPDS card no. 42-0216) and zeolite NaP1 ($\text{Na}_{3.6}\text{Al}_{3.6}\text{Si}_{12.4}\text{O}_{32}\cdot 14\text{H}_2\text{O}$, JCPDS card no. 39-0219) (Nchare et al., 2016; Fernández et al., 2008; Degennaro et al., 1991). These results substantiated the successful synthesis of HS and zeolite NaP1 via MWCT mode as the dominant crystalline phases for both methods.

In DHS method, when the temperature was adjusted to 80°C , the product was predominately amorphous and no diffraction was observed (Figure 4-3). As the temperature increased to 90°C , a few peaks with low relative intensity were observed. This indicates that a small degree of crystal growth occurred at low temperatures. Further increasing the temperature to 150°C remarkably increased the characteristic reflections corresponding to HS. These findings confirm that the increase in temperature improved the crystal growth of DHS zeolites.

The XRD patterns of the IFS zeolites (Figure 4-4) synthesized via MWCT mode showed higher intensity of zeolite characteristic reflections compared to DHS zeolites. It could be clearly seen that the intensity of the characteristic peaks correspond to HS (those observed at 2θ of 14.0° and 24.5°) decreased as the temperature increased in IFS method. This indicates that the crystal growth diminished in IFS method with the increase in temperature, despite the observations made for DHS zeolites.

Figures 4-3 and 4-4 showed that no new phases were observed in both methods as the temperature increased from 80 to 150°C via MWCT mode. As a result, HS and zeolite NaP1 were the most stable phases within the temperature range and the geopolymer network growth favored the formation of the nuclei corresponding to these two phases. The XRD patterns of the DHS zeolites

showed remarkably broader hump at low angles compared to those synthesized by IFS method. This indicates that IFS-synthesized zeolites had a much higher crystal growth efficiency compared to those DHS-synthesized materials via MWCT mode.

4.3.1.3. Zeolite production via MWCP Mode

Figure 4-5 depicts the XRD patterns of the zeolites synthesized by DHS and IFS methods via MWCP mode. Figure 4-5 showed that the products synthesized by DHS were predominantly

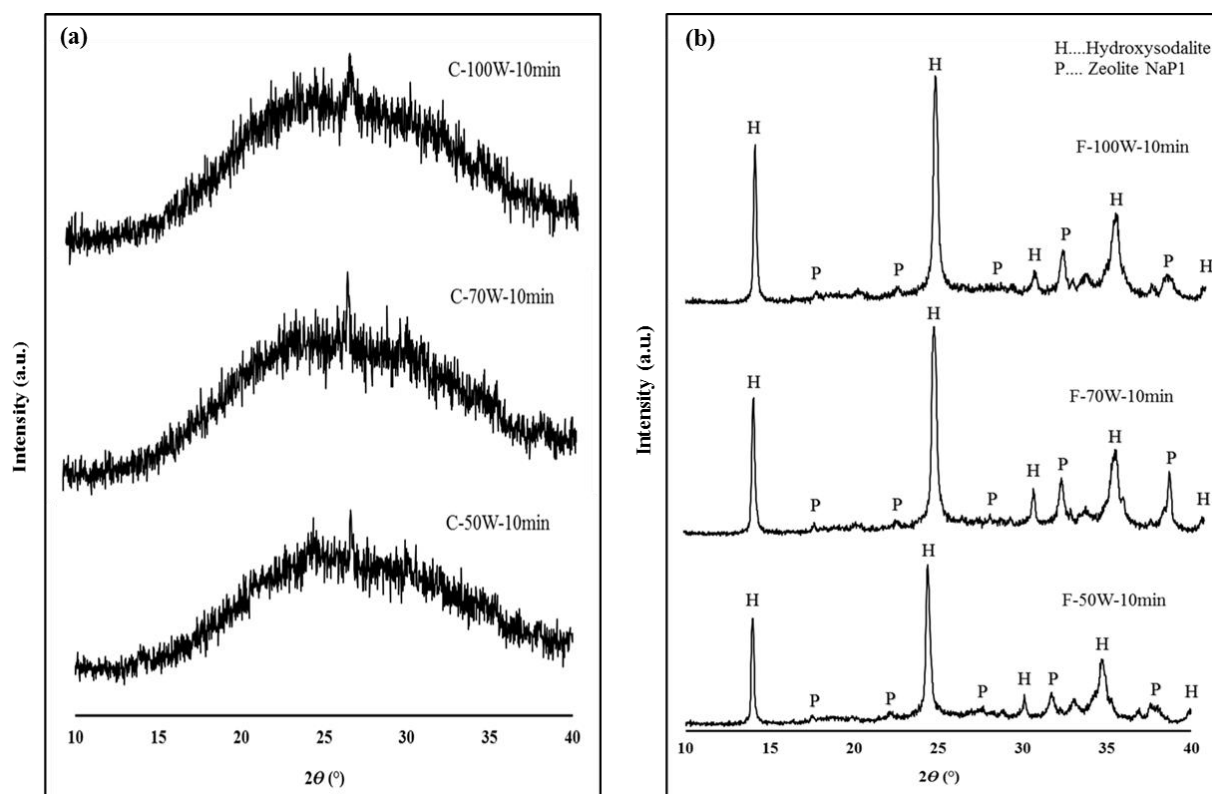


Figure 4-5. XRD patterns of the zeolites synthesized by (a) DHS and (b) IFS methods via MWCP mode

amorphous and a broad hump was observed in the patterns. However, the patterns for the products synthesized by IFS method showed much less broadened hump at low angles and diffractions with high relative intensities were observed. This indicates that the crystal growth efficiency of the IFS materials was much higher compared to those synthesized by DHS method via MWCP mode.

4.3.2. Phase Evolution

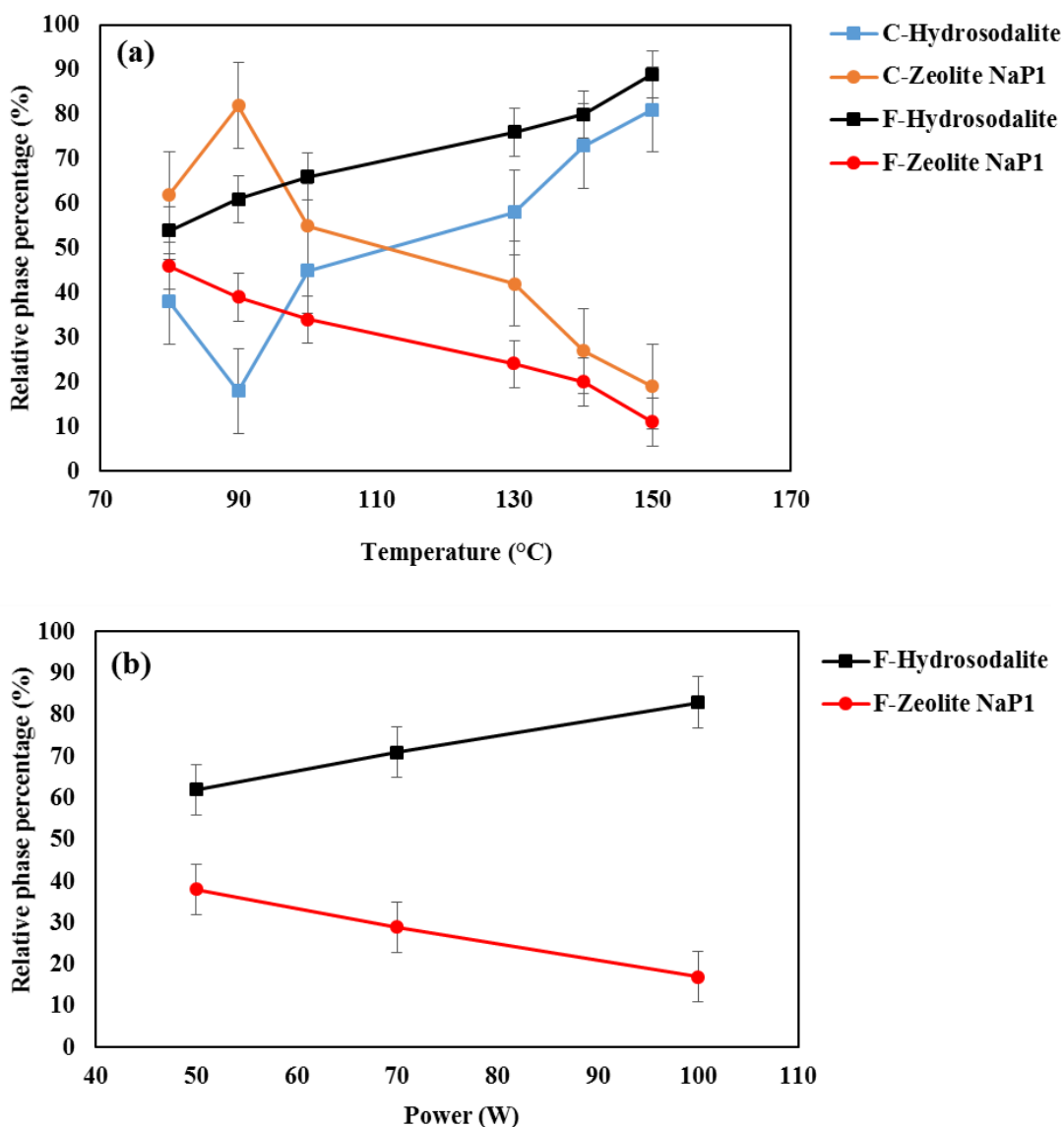


Figure 4-6. Phase evolution of the zeolites synthesized by DHS and IFS methods via (a) MWCT and (b) MWCP modes

Figure 4-6 illustrates the phase evolution as well as the relative phase percentages of the zeolites synthesized by DHS and IFS methods via MWCT and MWCP modes. Zeolites synthesized in DHS and IFS methods via MWCT mode showed an overall trend of the increase in HS phase fraction with the increase in temperature to 150°C (Figure 4-6a) while a decreasing trend for zeolite NaP1 was witnessed for both methods. The same evolution trends of HS and zeolite NaP1 were

also observed for the IFS zeolites synthesized via MWCP mode (Figure 4-6b). This indicates that the increase in temperature and power of radiation favors the nucleation of HS in the gel, as this phase is reportedly the most stable phase within the temperature range measured during the synthesis.

4.3.3. Relative Crystallinity

4.3.3.1. Zeolites synthesized via MWCT Mode

Figure 4-7 shows the variations in the intensity of the characteristic peak as well as relative crystallinity of the zeolites synthesized by DHS and IFS via MWCT mode. In this study, the relative amorphous phase percentage was obtained by calculating the ratio of the hump area of the zeolitic materials synthesized through MWCT and MWCP modes to that of the hump area in the most amorphous sample (starting WG powder considered as 100% amorphous, Figure 4-2). The relative crystallinity of the materials was then calculated from the relative amorphous phase percentages, as both are complementary values (Tarasi et al., 2013). The results showed that the relative crystallinity of the zeolites synthesized by IFS method via MWCT mode was much higher compared to the DHS zeolites within the temperature range. This indicates that IFS method provided materials with much higher crystal growth efficiency as compared to DHS synthesized zeolites. The maximum relative crystallinity of 80% for the IFS zeolites was obtained at 80°C. However, the DHS zeolites provided the minimum relative crystallinity of 10% at 80°C. Moreover, the DHS and IFS zeolites showed opposite trends for the relative crystallinity as the temperature increased to 150°C in MWCT mode (Figure 4-7). This could be attributed to higher ionic conductivity of the gel in IFS method compared to DHS method that may affect the crystal growth.

4.3.3.2. Zeolite synthesized via MWCP Mode

Figure 4-8 illustrates the trends of the intensity of the characteristic peak as well as the relative

crystallinity of the zeolites synthesized by DHS and IFS methods via MWCP mode. It was observed that the relative crystallinity of IFS zeolites was much higher compared to DHS materials. This much higher degree of crystal growth obtained by IFS zeolites is attributed to the application of cooling air jet (CAJ) to the vessel wall during the MWCP radiation mode. It is proposed that CAJ employment could improve the crystal growth by efficiently monitoring the temperature and pressure during the synthesis via MWCP mode. The relative crystallinity of IFS zeolites increased with the increase in power of radiation while a decreasing trend was observed for DHS zeolites. This could also be due to the variation of temperature and pressure in the vessel during the MWCP mode that may affect the crystal growth.

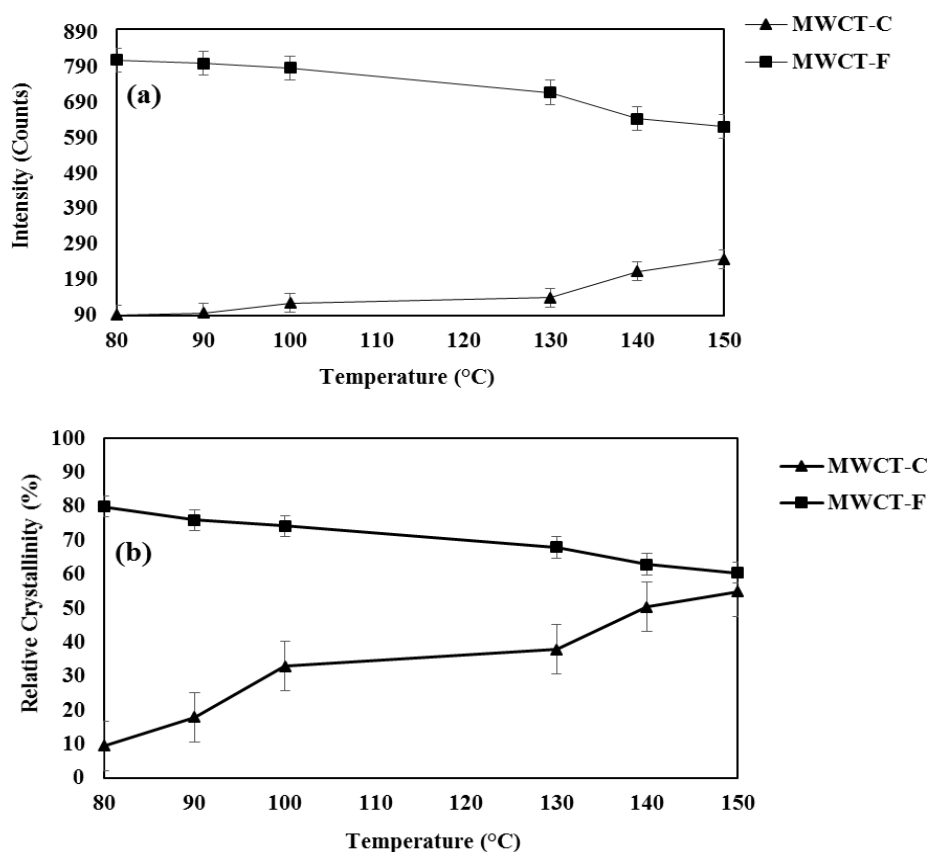


Figure 4-7. Variation of (a) the intensity of the characteristic peak and (b) relative crystallinity of zeolites synthesized by DHS and IFS methods via MWCT mode

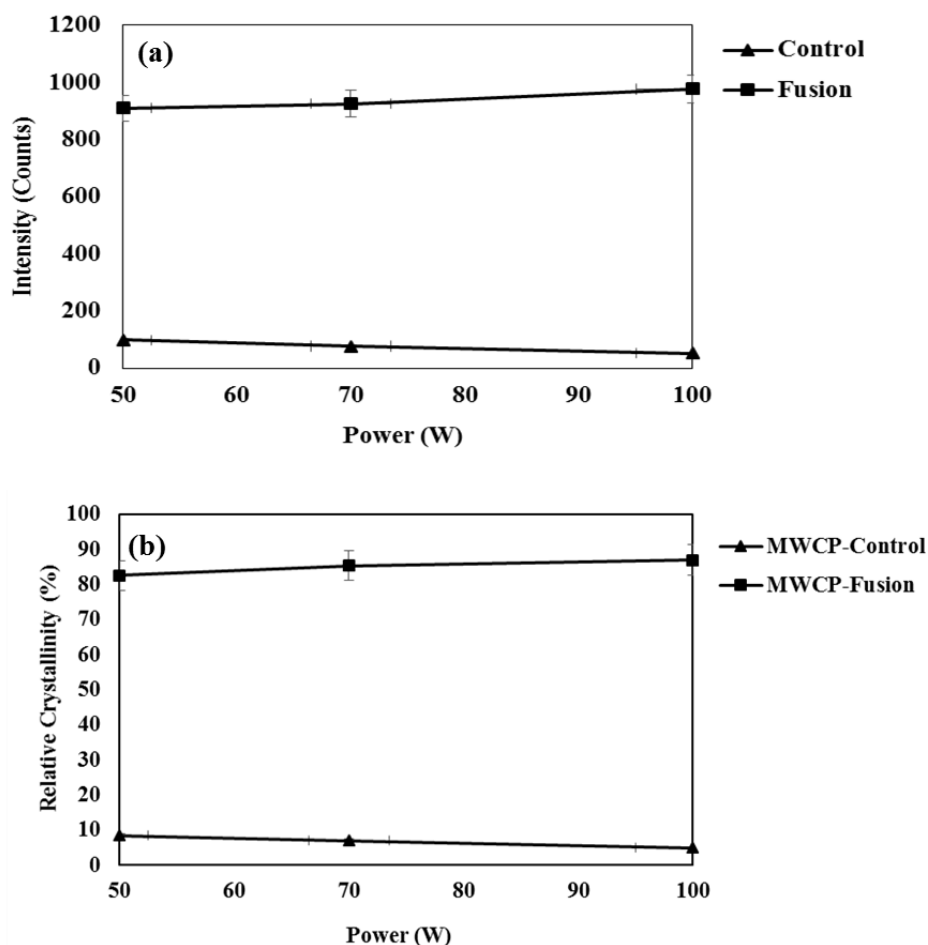


Figure 4-8. Variation of the (a) intensity of the characteristic peak and (b) relative crystallinity of zeolites synthesized by DHS and IFS methods via MWCP mode

4.3.4. Trends of Synthesis Temperature and Pressure

4.3.4.1. MWCT Synthesis Mode

Figure 4-9 shows the trends of the maximum vapor pressure measured in the reaction vessel during the MWCT synthesis mode for DHS and IFS methods. The vapor pressure within the vessel ranged between 18 and 94 psi for the DHS method as the temperature increased from 80 to 150°C. However, a higher vapor pressure range for IFS method between 80 and 210 psi was found within the vessel for the same temperature range. This confirms generation of higher vapor pressure in IFS method as compared to DHS method in the MWCT mode.

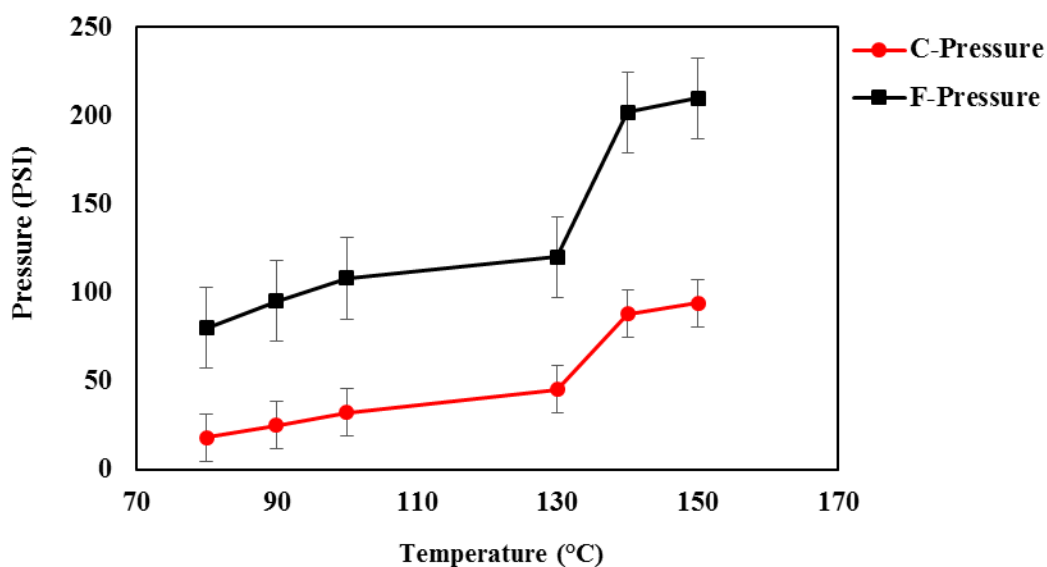


Figure 4-9. Maximum pressure measured during the MWCT synthesis within the reaction vessel for DHS and IFS methods

4.3.4.2. MWCP Synthesis Mode

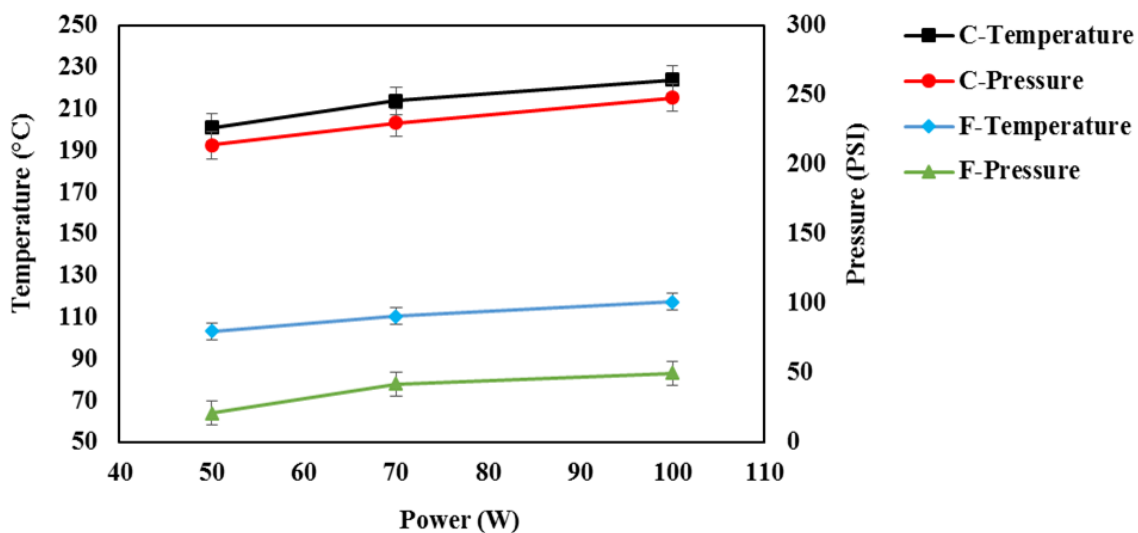


Figure 4-10. Maximum temperature and pressure measured during the MWCP synthesis within the reaction vessel for DHS and IFS methods

Figure 4-10 illustrates the trends of the maximum temperature and pressure measured in the reaction vessel during the MWCP synthesis mode for DHS and IFS methods. In DHS method, the

maximum temperature and pressure ranged between 201 to 224°C and 214 to 248 psi, respectively, as the power of radiation increased from 50 to 100W. However, due to the application of CAJ in IFS method, the maximum temperature and pressure ranged between 97 to 115°C and 21 to 50 psi, respectively. Therefore, these results evidently imply that the temperature overshoot and high vapor pressure generation were efficiently monitored in IFS method due to the CAJ impact as compared to DHS method through MWCP mode.

4.3.5. FTIR Results

FTIR spectroscopy is a very valuable technique for gaining the vibrational data to identify various kinds of functional groups in the materials. Therefore, WG, FWG, and the zeolites synthesized by DHS and IFS methods via MWCT mode were inspected by FTIR analysis and the results are presented in Figure 4-11. The FTIR spectrum of WG exhibits bands at 3475 cm^{-1} , 2358 cm^{-1} , 1646 cm^{-1} , 1024 cm^{-1} , 882 cm^{-1} , and 538 cm^{-1} . Based on literature, the band centered at 3475 cm^{-1} raised due to the O-H molecule bending and stretching vibrational modes as well as the silanol hydrogen group Si-OH stretching mode within the glass framework (Naresh et al., 2016). The characteristic band observed at 2358 cm^{-1} corresponds to the O-H bonds vibrational modes generated at non-bridging oxygen locations (Naresh et al., 2016). The band observed at 1646 cm^{-1} could correspond to the vibrational modes of O-H group as well as Si-O bridging oxygen asymmetric stretching vibration formed inside the tetrahedral units (Naresh et al., 2016).

The couple of bands observed over the range of 1100 cm^{-1} -500 cm^{-1} are attributed to the Si-O-Si vibrational mode in the matrix of SiO_4 tetrahedral structural cells (Kumar et al., 2010). However, there were no bands observed at 3475 cm^{-1} , 2358 cm^{-1} , 1024 cm^{-1} , and 882 cm^{-1} in FWG spectra as compared to WG. This could be attributed to the destruction of the WG structural framework after fusion step due to the penetration of liquid NaOH within the glass network.

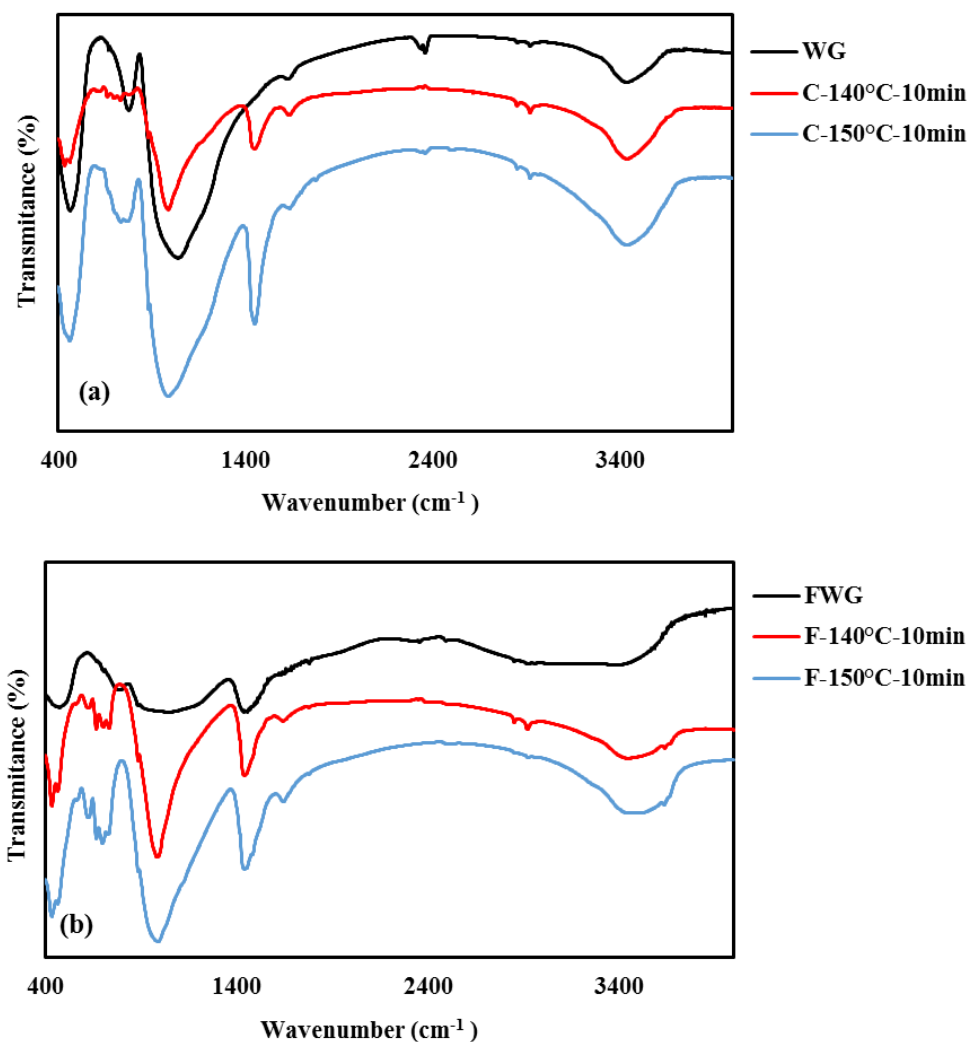


Figure 4-11. FTIR spectra of (a) WG as well as zeolites synthesized by DHS method and (b) FWG as well as zeolites synthesized by IFS method via MWCT mode

The FTIR spectra of the zeolites synthesized using DHS and IFS methods provided several characteristic bands in the areas 450-1100 cm⁻¹, 1653 cm⁻¹, and 3475 cm⁻¹. The peaks at 1022 cm⁻¹ correspond to the (Si, Al)-O asymmetric stretching internal vibration, those at 689 cm⁻¹ correspond to the (Si, Al)-O symmetric stretching internal vibration, and peaks at 467 cm⁻¹ correspond to the (Si, Al)-O bending internal vibration (Shoumkova and Stoyanova, 2013b). The band attributed to O-H also assigned at about 1653 cm⁻¹ (Sarria et al., 2006). A wide characteristic peak was also appeared at 3475 cm⁻¹, which was related to the OH stretching vibrational mode

formed in hydroxyl groups (Courtney et al., 2015). These results are consistent with the XRD phase identifications. The characteristic band that appeared at 2358 cm^{-1} on the WG spectrum was not observed on the zeolite spectrum, indicating the conversion of glass into zeolite.

4.3.6. EDX Results

Figure 4-12 shows the EDX analytical composition results of the WG, FWG, and the zeolitic materials synthesized using DHS and IFS methods. Elements including Al, Si, O, Na, Ca, K, and Mg were found in WG, FWG, and zeolites synthesized by both methods. EDX analysis confirms the presence of different metallic elements within the composition of WG and FWG.

The peak corresponding to C element in all EDX graphs is due to the use of the carbon tape as the sample holder. The results in Figure 4-12 (c) and (d) showed that the DHS zeolite Si/Al ratio was 8.2 while this ratio for the IFS zeolite was roughly 0.73. This indicates that the IFS zeolite could provide much better cation exchange capacity (CEC) and catalytic performance compared to the DHS zeolite.

4.3.7. SEM Results

SEM imaging was used in this study to provide information regarding the morphologies of the synthesized zeolites and to compare the crystal growth. Figure 4-13 shows the SEM images of the WG cullet, the FWG, and zeolites synthesized by DHS and IFS methods via MWCP mode. According to Figure 4-13 (c) and (d), no specific morphologies were observed for the DHS zeolites, which validates the XRD data. The XRD results showed that the mentioned material was predominately amorphous and this arises the probability that the structures shown in Figure 4-13 (c) and (d) could be amorphous gel. The images illustrated in Figure 4-13 (e) and (f) show the flower shape and aggregated needle-like morphologies associated with HS and zeolite NaP1, respectively. This also validates the XRD results obtained for the IFS material

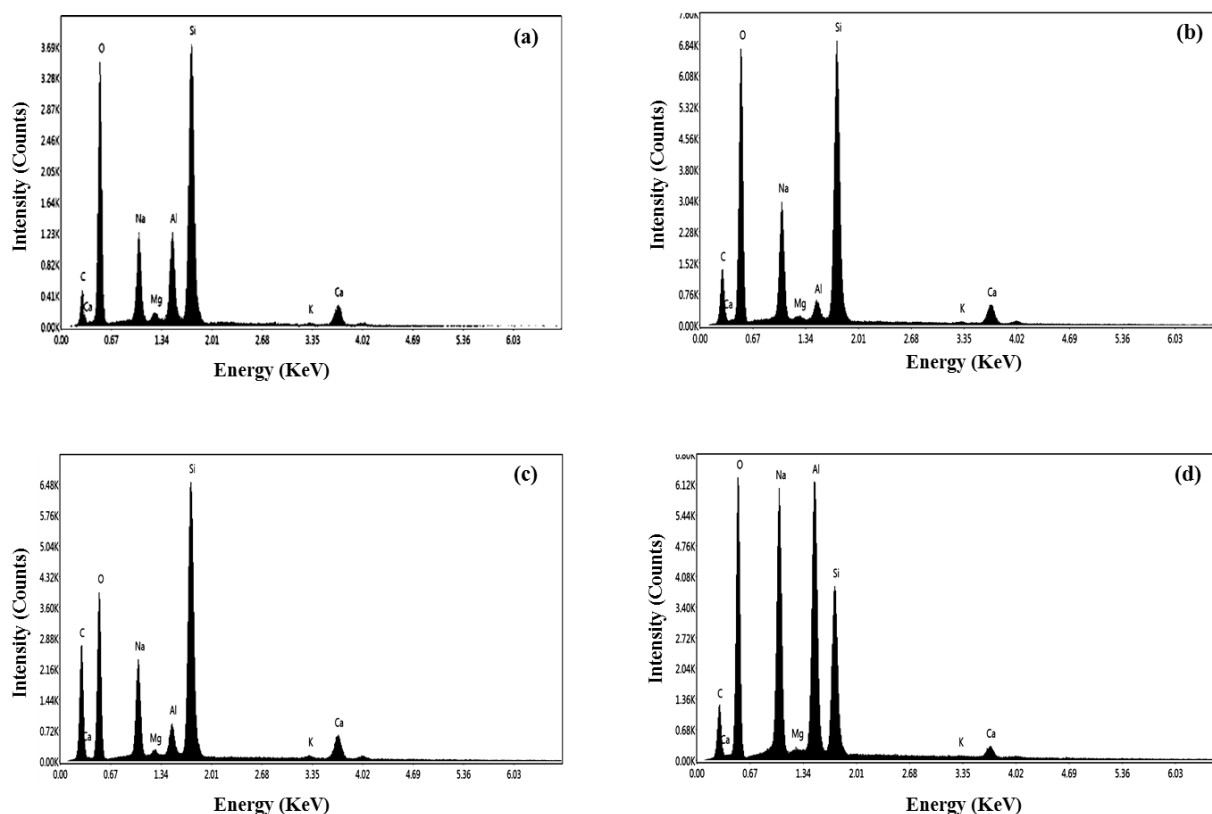


Figure 4-12. EDX analysis of elemental composition for (a) WG cullet, (b) FWG, (c) zeolite synthesized by DHS method, and (d) zeolite synthesized by IFS method

synthesized via MWCP mode. According to Figures 4-13 (e) and (f), it is theorized that the crystals nucleation and growth occurred on the amorphous gel surface, which could also be deposited on the surface of glass particles. This agrees with the recent findings that zeolite crystallites are generated via a heterogeneous crystallization (Inada et al., 2005).

4.3.8. TGA Results

The ability of a zeolite to adsorb water into its framework is an important trait. TGA results of the WG cullet, FWG, and the zeolites synthesized by DHS and IFS methods are shown in Figure 4-14. TGA results of the WG cullet showed a very small weight loss (<1%), while the weight loss

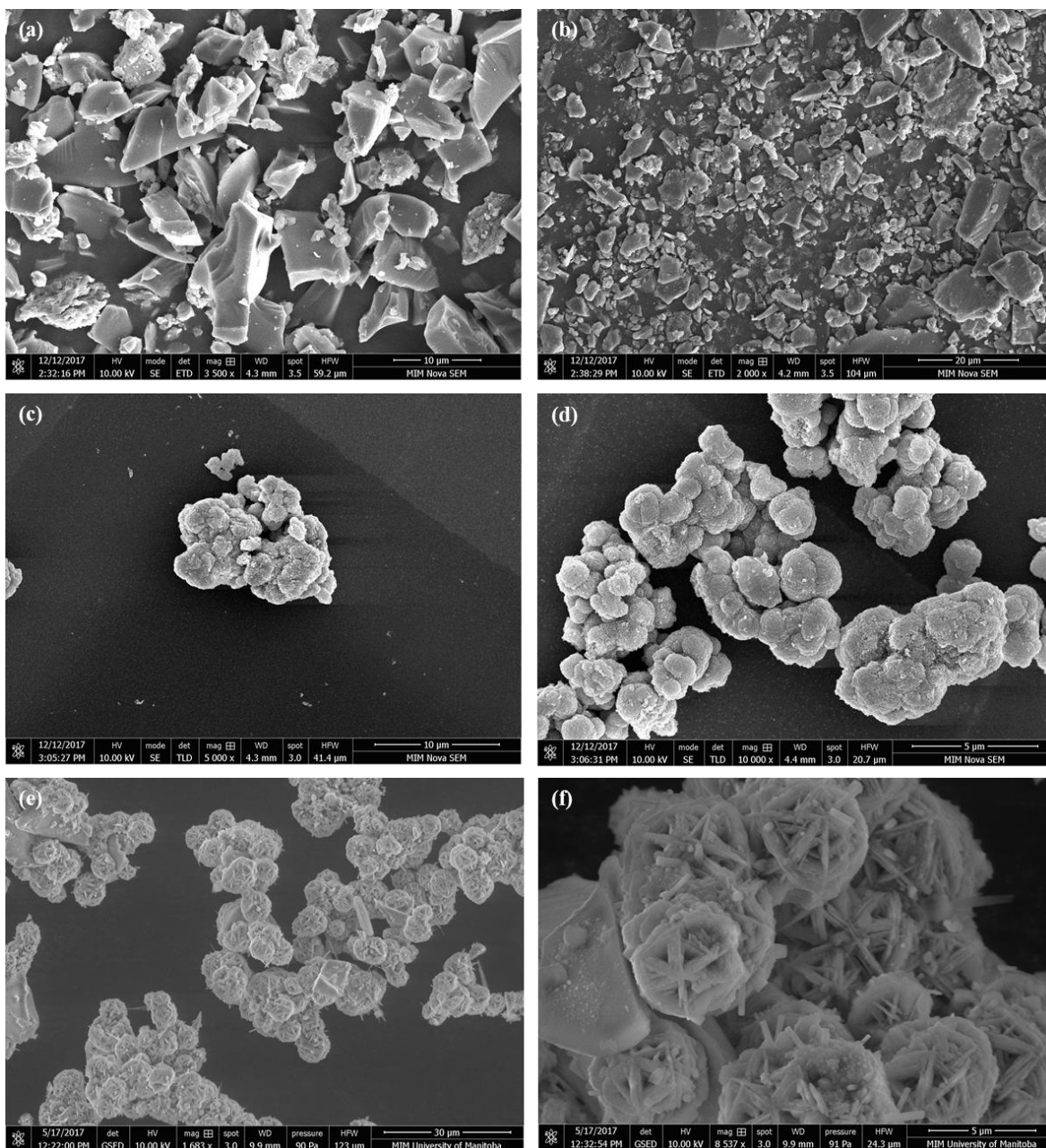


Figure 4-13. SEM images of (a) WG cullet; (b) FWG; (c) and (d) zeolite synthesized by DHS method; (e) and (f) zeolite synthesized by IFS method

of the FWG was roughly 5%. The moderate-slope weight loss and the heat flow variations are specific features of WG. These are assigned to the atmospheric moisture reversible sorption on the WG framework external surface and macropores. TGA data related to zeolites synthesized by DHS and IFS methods showed a weight loss of 5.8 and 9.1%, respectively. These values indicate that

the water content of the IFS zeolite was higher as compared to the DHS zeolite. As a result, TGA data validated the EDX results and confirmed the lower Si/Al ratio of the IFS zeolites compared to the DHS zeolites. The maximum weight loss for the DHS and IFS zeolites occurred at 83 and 62°C (Figure 4-14b). These two points of inflection were observed due to the vaporization of the adsorbed moisture content available inside the obtained zeolites capillary micropores (Bukhari et al., 2014).

4.3.9. Cation Exchange Capacity (CEC) Results

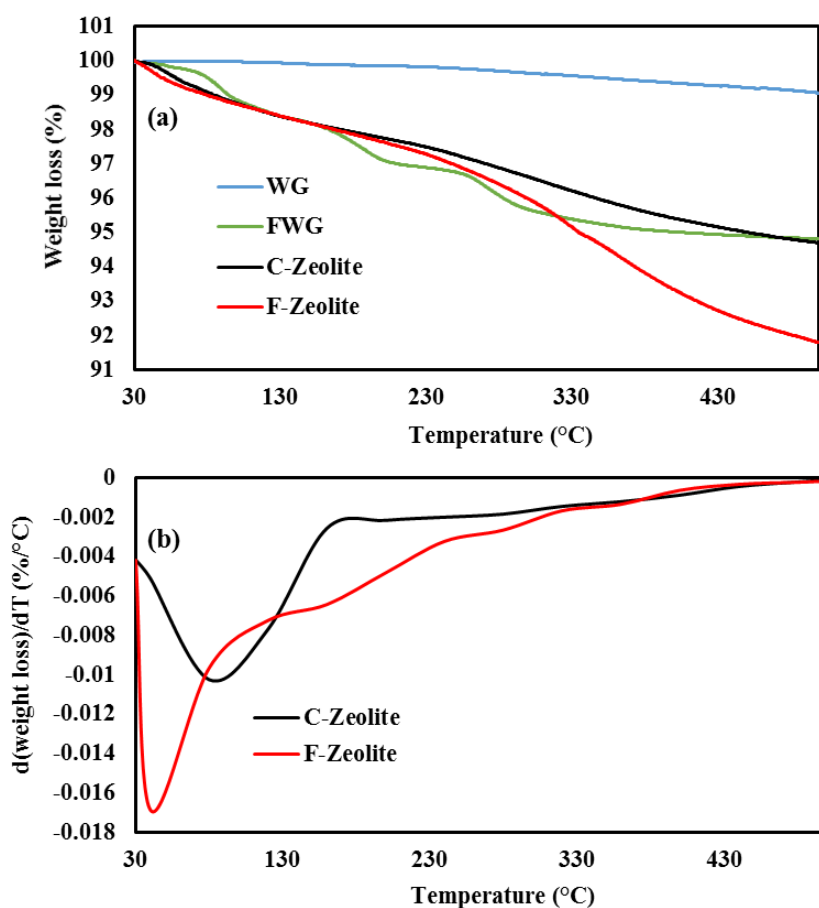


Figure 4-14. (a) TGA and (b) differential TGA of WG, FWG, DHS zeolite, and IFS zeolite

The chemical activity of zeolites is mainly determined by the measurement of their CEC as it strongly depends on the Si/Al ratio of the framework. Figure 4-15 shows the CEC values of WG,

FWG, and zeolites synthesized by DHS and IFS methods. The CEC values for the WG and FWG were 0.10 and 0.21 mol/g, respectively. The CEC values of the WG and FWG remarkably increased after the zeolitization process (Figure 4-15) to 1.78 and 2.19 mol/g for the DHS and IFS zeolites, respectively. Therefore, the CEC results also validated the EDX and TGA data, confirming that IFS zeolite provided lower Si/Al ratio and better ability of exchanging cations compared to DHS zeolite. The CEC values were in congruence to the zeolites synthesized from coal fly ash (Tanaka et al., 2006; Kazemian et al., 2005). This also shows that the zeolite synthesized by IFS method has a significant

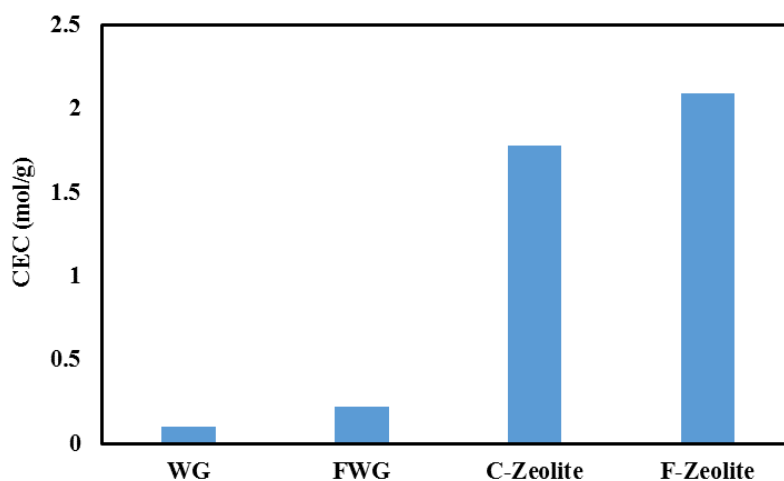


Figure 4-15. CEC values of WG, FWG, and zeolites synthesized by DHS and IFS methods

capability for the application in various environmental remediation purposes as a useful ion exchanger.

4.4. Discussion

4.4.1. Comparison of DHS and IFS Methods in Terms of Gel Growth

Results from XRD and relative crystallinity indicated that the IFS zeolites had higher crystal growth efficiency as compared with DHS zeolites. This could be attributed to the considerable release of soluble silicates into the reaction mixture in IFS method. It is proposed that in DHS

method, the presence of Al species in the initial gel would result in the absorbance of soluble aluminates on the surface layer (Si-enriched) of the WG particles. As a result, the surface layer of the glass particles is passivated by evading the hydroxyl ions. The mentioned phenomenon severely decelerates the Si release rate within the gel in DHS method (Rees et al., 2008). The adverse effect of soluble Al species could thus be the main reason of the low crystal growth performance in DHS method.

In contrast to DHS method, there are no soluble aluminates in the gel in IFS method at the time of Si release, which includes 2h stirring of solution after the fusion step and before the hydrothermal reaction, to passivate the surface layer of FWG particles. The active hydroxyl ions would then attack the surface layer of the FWG particles resulting in a high Si release. This provides abundant nuclei within the gel, and consequently higher crystal growth occurs during the IFS method. Therefore, the main advantage of IFS over DHS method could be the elimination of the inhibitory effect of soluble Al species on Si release. It should be noted that the destruction of WG framework by solid NaOH fusion that occurs at high temperature strongly affects the amount of Si release in IFS method (Bukhari et al., 2014).

4.4.2. Impact of Temperature and Pressure on Crystal Growth in DHS and IFS Methods

4.4.2.1. MWCT Mode

The relative crystallinity of the IFS materials decreased as the temperature increased while the relative crystallinity of the DHS zeolites increased (Figure 4-7). This opposite trend could be justified by explaining the difference in interaction of MW with the gel components in both methods. In DHS method, the primary gel is mostly Al-enriched and due to the surface passivation of the WG particles by aqueous Al species, release of Si and other metallic elements is

considerably retarded. Therefore, a slow dissolution of WG particles and low ionic conductivity within the gel occurs in DHS method.

However, in IFS method, a large amount of Si and other metallic elements available in FWG (confirmed by EDX analysis in this study, Figure 4-12) could dissolve into the reaction mixture without the inhibitory effect of soluble aluminates, as previously mentioned. This means that the IFS method provides higher ionic conductivity within the primary gel compared to DHS method. In another words, the interaction of the MW with the ionic gel could be more intensive in IFS method compared with DHS method within the same temperature range. This intensive interaction of the MW and ions present in the gel in IFS method generates high vapor pressure that may adversely affect the crystal growth. Therefore, higher temperature applied to the gel in IFS method generated an excessive vapor pressure that subsequently resulted in less crystal growth via MWCT mode (Figures 4-7 and 4-9). This also concurs with the literature findings. Watanabe et al. (1993) and Rezaei et al. (2016) also reported that the zeolite structure may be degraded in a high-temperature high-pressure environment.

4.4.2.2. MWCP Mode

According to Figure 4-8, the relative crystallinity of the DHS materials decreased while the relative crystallinity of the IFS zeolites increased with the increase in the power of radiation. This means that more irradiation power in DHS method provided a higher temperature overshoot and vapor pressure generation inside the vessel (Figure 4-10); thus, less crystal growth and more amorphous phase fraction was observed (due to the reasons previously explained). However, due to the application of CAJ in IFS method, the temperature and vapor pressure was monitored efficiently in the vessel providing less inhibitory effects on crystal growth. It is proposed that the application of CAJ cools down the vessel wall and consequently the excessive expected hot spot zones formed

inside the reaction mixture, and effectively monitors the temperature overshoot and high vapor pressure generation within the vessel (Figure 4-10). Accordingly in IFS method, the crystal growth improved as the radiation power increased (Figure 4-8).

4.5. Conclusions

In this study, WG cullet was converted to zeolites utilizing a single-mode MW radiation. Two conversion methods including DHS and IFS were studied by monitoring the temperature and power of radiation via MWCT and MWCP modes. The results showed that IFS was a successful synthesis method and produced zeolites with remarkably higher degree of crystallinity as compared to those synthesized by DHS method. The main reason of better synthesis performance in IFS method was attributed to the elimination of the inhibitory effect of aqueous Al species on Si release. EDX, TGA, and CEC data validated that IFS zeolites also provided better ability of exchanging cations and water holding capacity as compared with DHS zeolites due to a lower Si/Al ratio. It was observed that the temperature overshoot and high vapor pressure generation within the vessel adversely affected the crystal growth and produced materials with poor crystallinity. This was confirmed by the results obtained via MWCT and MWCP modes. It was shown that the temperature overshoot and high vapor pressure generation are strongly dependent on the ionic conductivity of the gel and the MW interaction with the gel components. The results also confirmed that the application of CAJ was an appropriate option for efficient monitoring of the temperature and vapor pressure inside the sealed vessel during radiation as it cooled the excessive hot spot zones generated. This technique effectively improved the crystal growth in IFS method as the power of radiation increased via MWCP mode.

Chapter 5. Microwave Synthesis of Zeolites from Waste Glass Cullet Using Landfill

Leachate as a Novel Alternative Solvent *

Type of experiment	Scientific contribution
Microwave heating synthesis	A.R. Majdinasab conducted all the synthesis experiments using microwave heating technique.
XRD	A.R. Majdinasab prepared the samples and did the data collection.
EDX	A.R. Majdinasab prepared the samples and A. Khan from the Manitoba Institute of Materials (MIM) did the data collection.
SEM	A.R. Majdinasab prepared the samples and A. Khan from the Manitoba Institute of Materials (MIM) did the data collection.
FTIR	A.R. Majdinasab prepared the samples and did the data collection.
TGA	A.R. Majdinasab prepared the samples and Y. Wroczynskyj from the Department of Physics and Astronomy did the data collection.
Cation exchange capacity (CEC)	A.R. Majdinasab prepared the samples and did the data collection.

*This chapter has been published as: Majdinasab, A., & Yuan, Q. (2019). Microwave synthesis of zeolites from waste glass cullet using landfill leachate as a novel alternative solvent. *Materials Chemistry and Physics*, 223, 613-622.

This chapter was fulfilled with the main objectives including: a) reusing a hazardous waste stream such as landfill leachate towards the synthesis of value added zeolites as an alternative aqueous phase and exploring its impact on types, quantities, and properties of zeolitic phases compared to the deionized water-based zeolites; b) investigating the influence of microwave interaction with the cations released into the gel by the landfill leachate on the crystallinity of the zeolites produced in comparison with deionized water-based zeolites.

The results obtained in this chapter contributed to the main objectives as they showed that zeolites synthesized by landfill leachate as the solvent exhibited superior properties in terms of crystallinity, cation exchange and water holding capacities. This chapter further contributed to the main objectives as it confirmed that higher concentration of Na^+ in the landfill leachate gel without filtration favored the formation of higher zeolite NaP1 portion compared to the deionized water. This chapter also found the higher ionic conductivity of the landfill leachate-based gel as the main parameter contributed to the superior crystallinity of the zeolites synthesized by microwave radiation.

Abstract

The present work investigated the microwave (MW) zeolitization of waste glass cullet using landfill leachate as a new potential solvent. The leachate-based zeolites were synthesized in two sets, one with metal precipitation and filtration (F-zeolite) and the second one with unfiltered metal precipitates (UF-zeolite). These two cases were compared with reference zeolites produced using deionized water (D-zeolite) in terms of their characteristics. Different characterization techniques were used including XRD, EDX, SEM, FTIR, TGA, and cation exchange capacity (CEC). Presence of cations other than Na^+ in leachate elevated the generation of hot spot zones and synthesized highly crystalline zeolites using unfiltered leachate. Substantial reduction in Na^+ concentration due to the solid filtration also favored the production of a roughly single-phase hydroxysodalite (HS) and suppressed zeolite NaP1 formation using filtered leachate. Deionized water also produced a small fraction of zeolite NaP1 due to the lower Na^+ content compared to unfiltered leachate. Zeolite synthesized using unfiltered leachate was also superior in cation exchange and water holding capacities due to its least Si/Al ratio as confirmed by EDX, TGA, and CEC results. The results from this study contribute to shed light on the efficiency of leachate application for large-scale zeolite synthesis in future prospect.

5.1. Introduction

Zeolites are hydrated crystalline aluminosilicates comprising alkaline and alkaline earth metals with regular internal cavities smaller than 2 nm. Due to their thermal, chemical, and mechanical stability, zeolites have found a wide range of industrial applications in oil and gas industry, soil remediation, and water purification (Czaja et al., 2009). Although conventional zeolite synthesis procedures involve the utilization of the pure chemicals, the utilization of various waste residues including rice husks, paper sludge ash, and coal fly ash has also been reported as alternative precursors for synthesis purposes (Prasetyoko et al., 2006; Wajima, 2017; Cardoso et al., 2015; Belviso, 2017).

Utilization of wastes such as coal fly ash may elevate certain risks, as these residues mostly contain toxic elements including Cd, Pb, Hg, and Cr (VI). This may restrict the wide application of such precursors to synthesize zeolites (Terzano et al., 2015). On the other hand, zeolite synthesis using pure chemicals could also be cost-prohibitive, making the final products economically unfeasible for agricultural and environmental applications. Hence, new cost-effective precursors are required for the clean zeolite production to satisfy the large-scale industrial demands for such materials.

Waste glass (WG) cullet retrieved from beverage bottles is readily available through separate collection systems of domestic solid wastes, and is predominately free of the potential toxic elements. Today, most WG recycling processes occur at extremely high temperatures (up to 1600°C), according to the glass composition (Sasai et al., 2008). As a result, high-energy consumption and greenhouse gas generation are the main drawbacks of these methods. The best solution for this problematic challenge is to convert the WG cullet into a highly value-added product such as zeolite. Since WG cullet is mostly composed of SiO₂, it could have a wide potential application as a starting feedstock for zeolite synthesis.

Nowadays, use of novel alternative energy sources such as microwave (MW) radiation has extensively blossomed for zeolite synthesis from silica-alumina gels. This is mainly due to the great impact of MW radiation on reducing induction period and increasing the nucleation rate (Behin et al., 2014; Bukhari et al., 2015; Sabouni et al., 2010; Chindaprasirt et al., 2013). MW radiation offers several benefits over conventional heating (CH) techniques for the synthesis of zeolites including elimination of by-products, shortening the crystallization time, providing narrower size distributions, producing various morphologies, and accelerating the nucleation period (Ansari et al., 2014; Fukasawa et al., 2018; Aldahri et al., 2017; Navarro et al., 2017). By elevating the normal boiling point of the reaction medium, MW radiation can also initiate superheating conditions for synthesis, if the vessel attains high pressure (Bukhari et al., 2015).

Typical zeolite synthesis procedures using alkaline hydrothermal processes require the consumption of a large volume of water. Behin et al. (2016) reported that synthesis of one metric ton of zeolite from coal fly ash requires 20 metric tons of fresh water. So far, most studies have focused on utilizing deionized (DI), distilled, or industrial water for the synthesis purposes, while a few cases have employed different water sources. One such study by Belviso et al. (2009) produced zeolite X using coal fly ash and seawater as the solvent. Their results showed that the production yield was higher using seawater compared to distilled water at different synthesis temperatures. In a different study, Hussar et al. (2011) utilized a by-product of an aluminum etching process to synthesize zeolite A by using a hydrothermal process. They reported that a higher crystallization temperature and prolonged reaction time favored zeolite A formation. Another study by Musyoka et al. (2011) investigated the effect of utilizing industrial waste brine solution to synthesize zeolites using coal fly ash. The brine contained high concentrations of Na and K, which resulted in the formation of hydroxysodalite. The same research group further utilized two types of mine waters, acid and circumneutral, retrieved from coal mining process

instead of pure water to synthesize zeolite Na-X and Na-P1 from coal fly ash (Musyoka et al., 2013). The circumneutral mine source favored the synthesis of zeolites Na-X and P while the utilization of acidic mine drainage resulted in the production of hydroxysodalite zeolite. In another study, Behin et al. (2014) used a liquid waste stream obtained from plasma electrolytic oxidation to synthesize zeolite A from coal fly ash. The synthesized zeolite had a comparable BET surface area, water content, and cation exchange capacity to that produced from distilled water.

The aforementioned studies show the wide variety of water sources that have already been utilized to produce zeolites. However, to the best of our knowledge, there is no reported study in the literature regarding the utilization of landfill leachate as an alternative source of water for zeolite synthesis. Therefore, utilizing landfill leachate as an alternative solvent to synthesize zeolites would be the main novelty of this study.

Landfill leachate is generated when water percolates a landfill soil cover and may contain bacteriological constituents, soluble organic, inorganic, suspended solids, different types of cations and heavy metals (Kjeldsen et al., 2002). As a result, it could potentially present various environmental hazards while the treatment process could be difficult and costly due to leachate's complex nature. A substantial portion of the landfilling expenses corresponds to the leachate treatment. This issue has led to a wide-scale research on investigating different methods to treat leachate (Rivas et al., 2004; Ghafari et al., 2009; Turan and Ergun, 2009). In order to reduce the adverse impact of landfill leachate on the environment, potential utilization of this liquid waste stream towards the synthesis of value-added products like zeolites requires further exploration.

The utilization of such a waste stream could also be a solution for large water demand requirement for zeolite synthesis industry. Therefore, the main objective of this study was to investigate the effect of using landfill leachate instead of deionized water on types and quantities of zeolites

synthesized from WG cullet by MW radiation. The effect of the MW interaction with landfill cations on the crystallinity of the synthesized zeolites was also studied.

5.2. Materials and methods

5.2.1. Materials

WG, in cullet form, was retrieved from the Manitoba Liquor and Lotteries recycling plant (Manitoba, Canada). The cullet was first passed through a 30-mesh sieve (0.595 mm) and then ball milled using a Laboratory Mill (MiniCer NETZSCH, Germany) to produce very fine particles. Briefly, 10 g of the sieved WG were added to 200 mL of deionized (DI) water and ball milled in a rotating chamber containing 30 mm spherical ZrO_2 beads at a rate of 400 rpm for 40 min. The resulting suspension was kept overnight after milling at room temperature to settle the glass phase, and the supernatant was then discarded. The settled glass phase was oven-dried at 70°C for 24h, and then ground using a mortar and pestle to provide a uniform and well-separated glass powder. The leachate was collected from the Brady Road Landfill, Winnipeg, Canada. A Grade 415 Filter Paper (VWR International, Mississauga, ON) was used to remove the residual particulate matter from leachate upon collection. Analytical grade chemicals like sodium aluminate ($\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:3\text{H}_2\text{O}$; Sigma-Aldrich, USA) and sodium hydroxide (NaOH; Alphachem Limited, Mississauga, Canada) were used as-received.

5.2.2. Zeolite synthesis procedure

The WG cullet zeolitization was carried out by a tow-step alkaline hydrothermal treatment in the following way.

For leachate synthesis experiments, 1 g of WG powder and 0.4 g of NaOH granules (NaOH/WG ratio of 0.4) were dissolved into 20 mL of leachate. As the pH of solution increased (required for Si release) by the addition of NaOH, metal hydroxides present in leachate precipitated.

Accordingly, two sets of experiments were conducted. In one set, the leachate solution was filtered through a 1- μ m Filter Paper (Fisher Scientific, Toronto, Canada) (fine-filtered) while in the second set the leachate solution remained unfiltered. The WG dissolution (Si release) and metal precipitation were achieved by stirring the mixture at room temperature for 20 h. Next, 1.41 g of NaAlO_2 was added to each of the mentioned leachate-based solutions and the reaction mixture was aged for 2h.

Subsequently, the mixtures were transferred into a 25 mL sealed borosilicate glass reaction vessel and exposed to MW radiation. The crystallization was carried out using a self-adjusting MW apparatus (2.45 GHz, CEM Corporation, Discover, USA). In this process the power and temperature were automatically monitored by constant temperature (MWCT) and constant power (MWCP) modes. In the former, the temperature was kept constant with the adjustment of MW irradiation power; while, in the latter, the synthesis was performed at constant power. The radiation time for both MWCT and MWCP modes was set at 10 min. The synthesis temperatures used in MWCT mode were 80, 100, 130, and 150°C and the power of radiation used in MWCP mode was stabilized at 50, 70, and 100 W. The temperature and pressure measurements were taken using an infrared pyrometer and a pressure sensor installed in the MW cavity. The system contained an MW generator, a heating chamber (cavity), and a laptop to record the temperature, pressure, and power profiles. After the crystallization period, the resultant powder was filtered, washed thrice with DI water, and then oven-dried at 70°C overnight.

Another set of experiments were also conducted to synthesize a zeolite as a reference using DI water with the same experimental procedure mentioned above (except the metal precipitation and filtration steps due to the low ionic conductivity of DI water). This step was conducted to provide a comparison with the zeolites synthesized from the leachate. In this study, zeolites synthesized by

fine-filtered leachate, unfiltered leachate, and DI water are labeled as F-zeolite, UF-zeolite, and D-zeolite, respectively. The flow diagram of different stages involved in MW zeolitization of WG using leachate-based and DI water-based gels is illustrated in Figure 5-1.

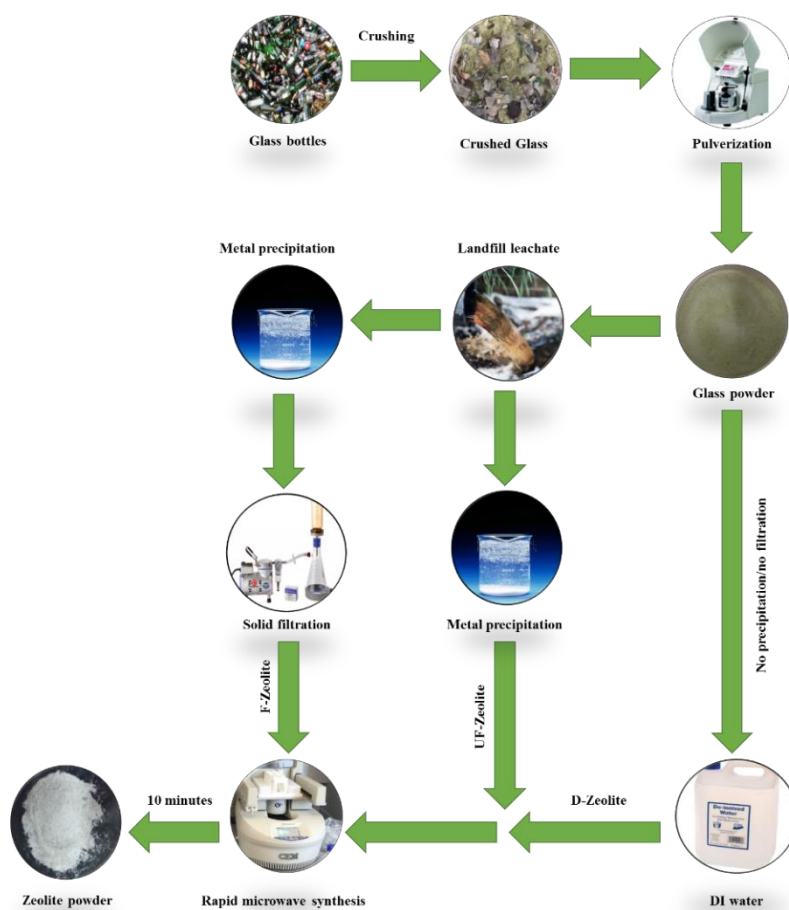


Figure 5-1. Flow diagram of different stages involved in WG conversion into zeolite using landfill leachate and DI water-based gels

5.2.3. Characterization of zeolites

Different analytical techniques were used to characterize the synthesized zeolites. X-ray diffraction (XRD) patterns were collected under ambient conditions with samples on a zero-background quartz slide. Data was collected using a diffractometer (D8 ADVANCE Bruker, WI,

USA) with $\text{CuK}\alpha$ (average $\lambda = 1.5418 \text{ \AA}$) over the range of $10^\circ < 2\theta < 40^\circ$. All the samples were normalized as the slide contained a 1-mm hole to adjust the zero background for all specimens. Phase matching analyses for all the products was done using DIFFRAC.SUITE EVA software and the best options offered by the phase matching software were selected. The results were corroborated with literature and reference patterns available in the crystallographic databases (Ansari et al., 2014; Bac et al., 2010). The relative phase percentages (phase fraction) for each phase available in the synthesized products were obtained using EVA software. The calculation was based on the ratio of the crystalline peak area of each matched phase to the total peak area in a pattern. In this method, the characteristic line for each phase was first scaled to 100% while other peaks were scaled relative to that value. The software then calculated the aforementioned ratio (phase fractions). The crystallite size of the samples was calculated according to Scherrer's equation (Belviso et al., 2009).

Scanning electron microscope (SEM) (JSM-6701F, Hitachi, Japan) operating at 10 kV accelerating voltage was used to study the morphology of the crystals. Compositional analysis for the WG cullet and synthesized zeolites was conducted using an energy dispersive X-ray spectrometer (EDX) (JSM-6701F, Hitachi, Japan). The Fourier transform infrared (FTIR) spectra of the samples were recorded using a spectrometer (GX FTIR, Perkin Elmer Spectrum, Mass, USA) with a scan range of $400\text{--}4000 \text{ cm}^{-1}$ by pelleting the sample powder with KBr. Thermogravimetric (TGA) measurements were taken by a thermal analyzer (TGA-7, Perkin Elmer, Mass, USA). The samples were heated in the range of 20°C to 400°C at a rate of $1^\circ\text{C}/\text{min}$ under argon gas.

Cation exchange capacity (CEC) of the samples was measured using NH_4Cl saturation method as proposed by Bain and Smith (1987). Briefly, 1 g of the sample was added to 50 mL of 1M NH_4Cl aqueous solution (pH 7, saturated with NH_4^+ ion). The mixture was stirred and allowed to reach

the equilibrium. Next, the mixture was centrifuged and the supernatants of all samples were collected for further analyses. The collected supernatants were diluted twice to adjust the concentration within the detection limit of the apparatus. The ammonium ($\text{NH}_4^+\text{-N}$) concentration of the diluted samples was measured using a flow injection analyzer (FIA) (Quick Chem 8500, LACHAT Instruments, USA) with the detection limit of 0.2 mg/L. The concentration of the main elements available in the leachate was measured using an inductively coupled plasma Atomic Emission Spectrometer (ICP-AES) (Optima-3300, Perkin-Elmer, USA).

5.3. Results and Discussion

5.3.1. XRD Results

5.3.1.1. Zeolite production via MWCT Mode

Figures 5-2 to 5-4 illustrate the XRD patterns of the D-, F-, and UF-zeolites synthesized via MWCT mode, respectively. The characteristic peaks observed at 2θ ranging from 10° to 40° matched with those for Hydroxysodalite (HS) ($\text{Na}_6(\text{AlSiO}_4)_6 \cdot 6\text{H}_2\text{O}$, JCPDS card no. 42-0216) and zeolite NaP1 ($\text{Na}_{3.6}\text{Al}_{3.6}\text{Si}_{12.4}\text{O}_{32} \cdot 14\text{H}_2\text{O}$, JCPDS card no. 39-0219) (Visa, 2016; Esaifan et al., 2017). A broad hump was observed at 80°C for all the zeolites (D, F, and UF) at 2θ between 15° and 40° . This indicates poor structural order of the gel for all three zeolites and the large fraction of remaining unreacted glass phase. This is due to the employment of low reaction temperature that was not appropriate for providing well structural order in the amorphous gel. Increasing the temperature to 100°C reduced the broadened hump corresponding to the amorphous phase and promoted the growth of zeolite crystalline peaks. This demonstrates the key role of temperature in zeolite crystallization (Figures 2-4). As the temperature further increased to 150°C , the characteristic peaks corresponding to HS gradually grew stronger for D, F, and UF-zeolites. This indicates HS as the most stable phase produced over the entire temperature range. The increase in temperature did not affect the type of zeolites produced; however, it yielded more HS for all

samples. According to Figures 5-2 to 5-4, the main diffraction peaks corresponding to zeolite NaP1 at 2θ of 17.9° , 21.6° , and 27.8° were detected stronger in UF-zeolite and weaker in D-zeolite while they were not observed in F-zeolite patterns. This could be attributed to the variation of Na^+ concentration that occurred in the reaction mixture of leachate and DI water-based gels. This difference in Na^+ concentration is due to the cations' precipitation and filtration in F-zeolite sample, precipitation and no filtration in UF-zeolite, no precipitation and no filtration in D-zeolite sample (since DI water contains negligible concentration of Na^+) .

5.3.1.1. Zeolite production via MWCP Mode

Figures 5-7 depict the XRD patterns of the D-, F-, and UF-zeolites synthesized via MWCP mode, respectively. In all three zeolites, the characteristic peaks of the main phase, i.e. HS, gradually increased with the increase in radiation power. This indicates that additional supply of radiation power improved the structural order of the gel and generated more zeolite nuclei. Similar to MWCT mode, the main diffraction peaks of zeolite NaP1 at 2θ angles of 17.9° , 21.6° , and 27.8° in fixed power mode were missing in F-zeolite patterns. The same reflections were weak in D-zeolite and relatively strong in UF-zeolite patterns. The main reason for these observations could be the variation of Na^+ concentration in the leachate and DI water reaction gels, as explained previously. Phase matching analysis shown in Figures 5-2 to 5-7 (MWCT and MWCP modes) demonstrated that the utilization of both leachate and DI water resulted in the synthesis of the same phase mixtures. However, the utilization of leachate instead of DI water affected the crystallinity of the samples and quantities of the HS and zeolite NaP1 phases. The effect of leachate on the

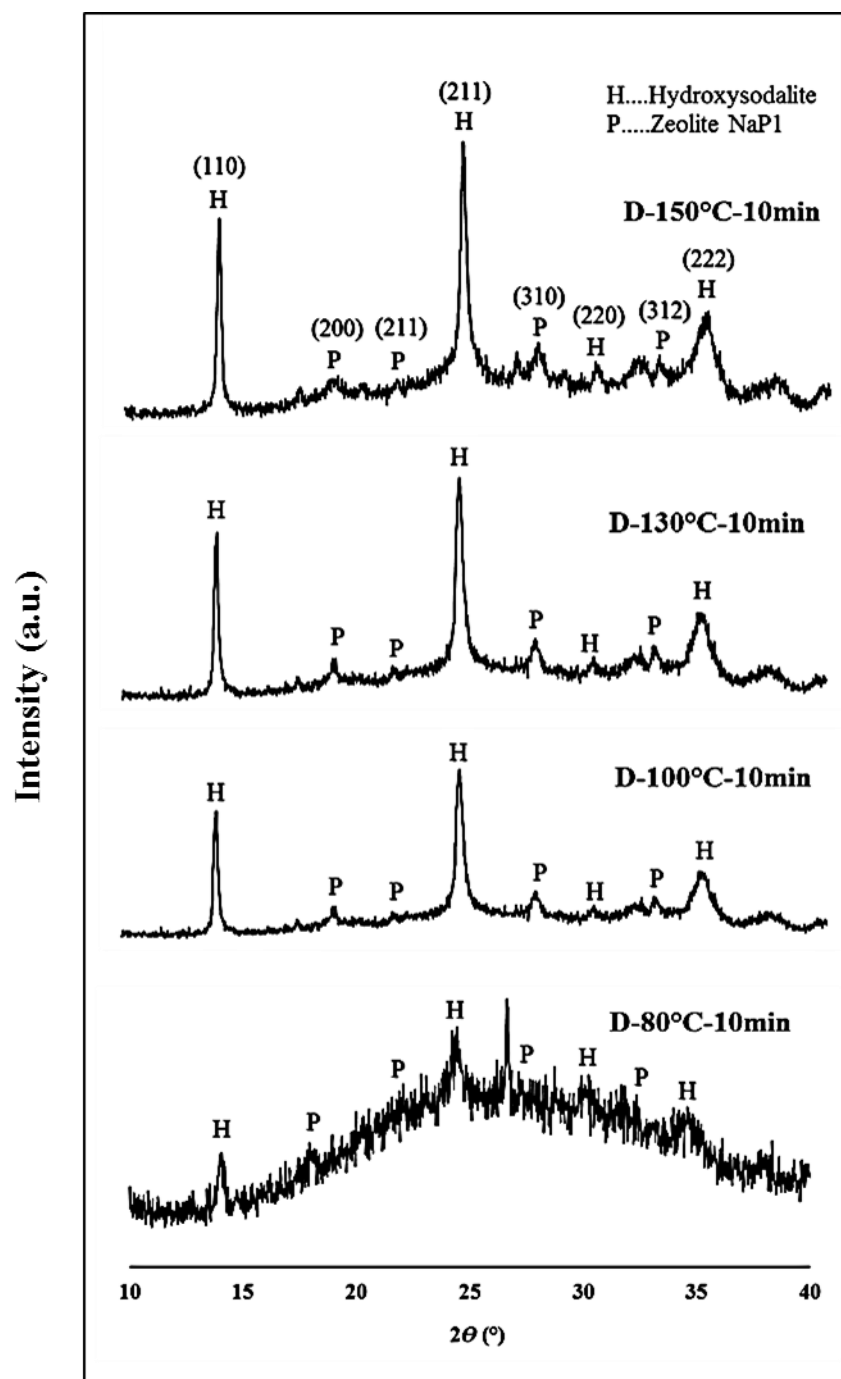


Figure 5-2. XRD patterns of the D-zeolites synthesized via MWCT mode

crystallinity of the zeolites could be attributed to the higher ionic conductivity of leachate-based

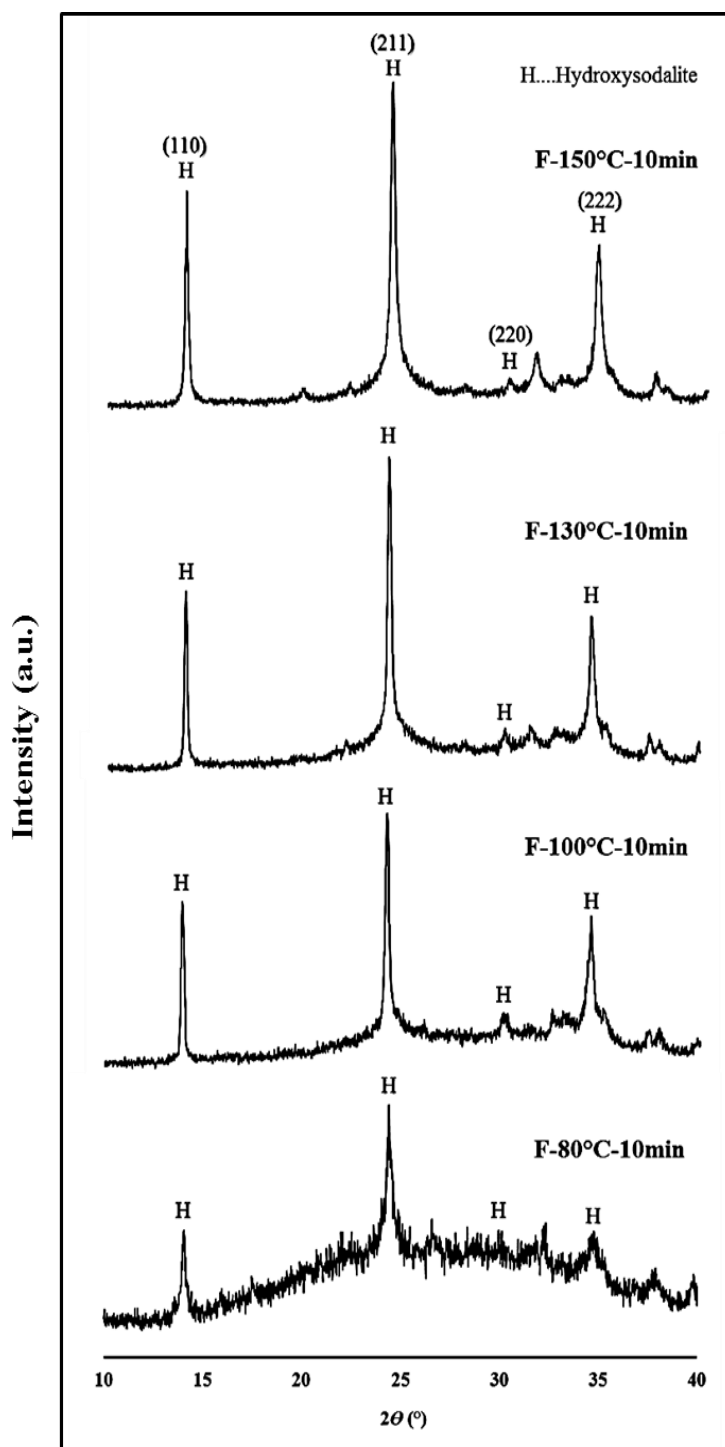


Figure 5-3. XRD patterns of the F-zeolites synthesized via MWCT mode

gel. This is mainly due to the presence of various cations other than Na^+ in leachate. The effect of leachate on HS and zeolite NaP1 fractions could be assigned to the variation of the Na^+ cation

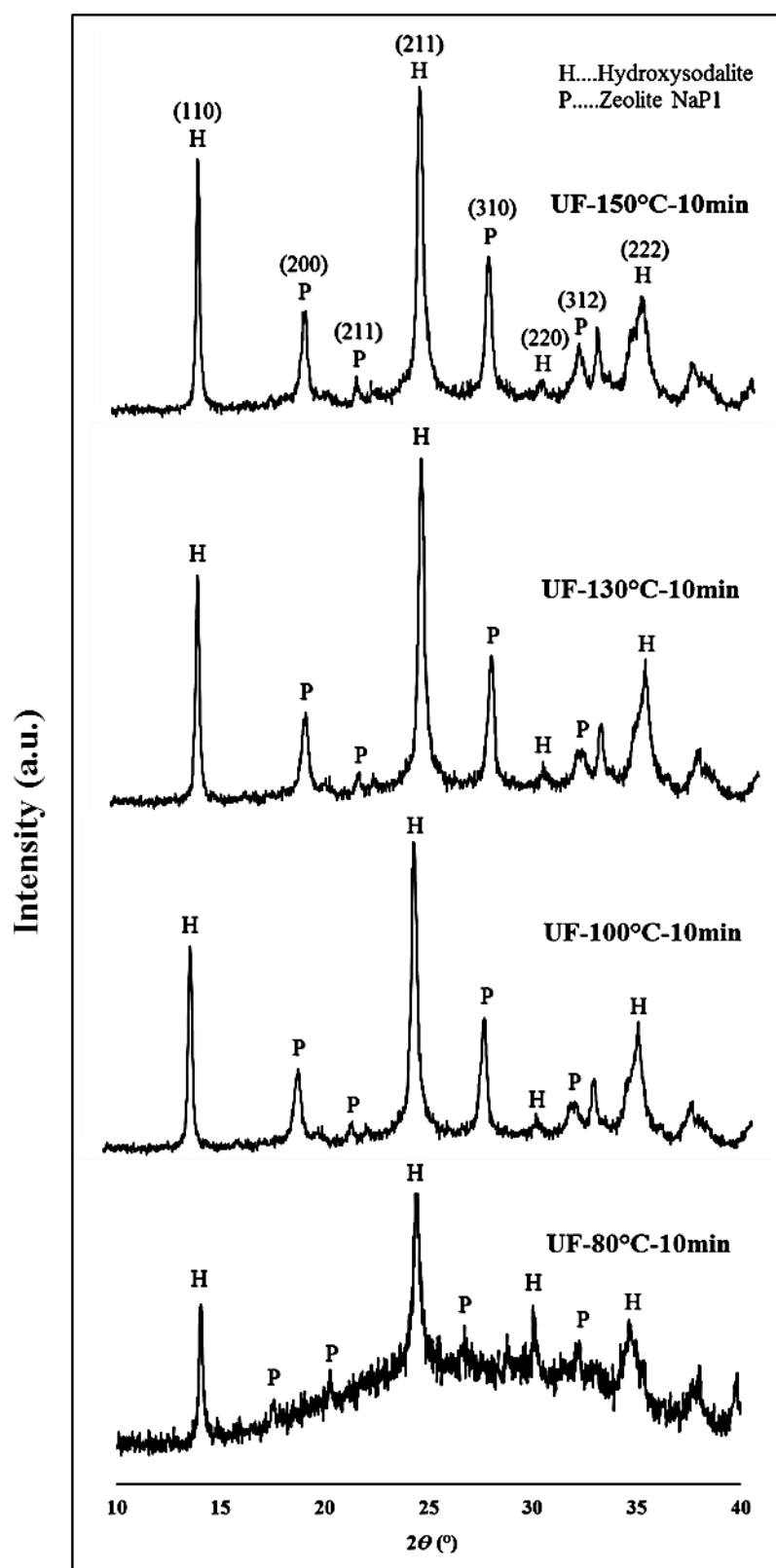


Figure 5-4. XRD patterns of the UF-zeolites synthesized via MWCT mode

content in leachate-based gel as compared to DI water-based gel. The average crystallite size of

the zeolites synthesized using MWCT and MWCP modes was approximately 44nm, based on Scherrer formula.

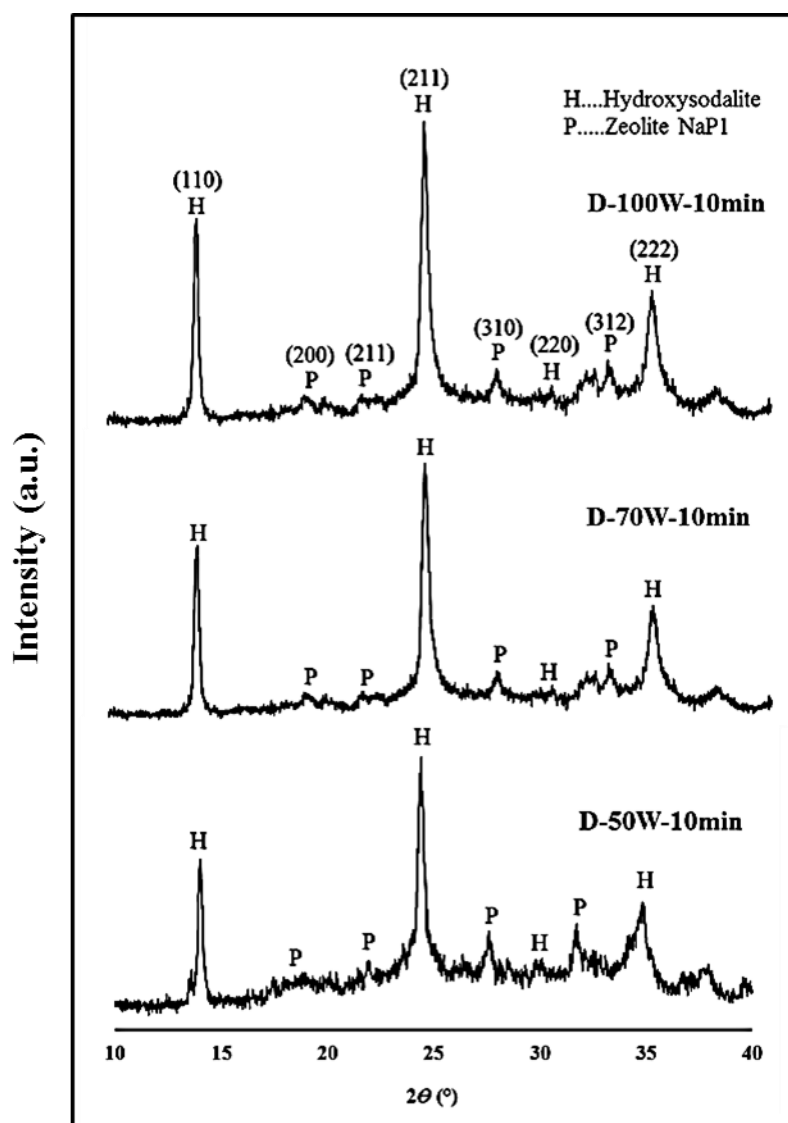


Figure 5-5. XRD patterns of the D-zeolites synthesized via MWCP mode

5.3.2. Relative crystallinity results

Figures 5-8(a) and (b) depict the variation in the relative crystallinity of D-, F-, and UF-zeolites as a function of temperature and power of radiation. In this study, the relative amorphous phase percentage was obtained by calculating the ratio of the hump area of the zeolite samples to that of

the hump area in the most amorphous sample (starting WG powder considered as 100% amorphous, Figure 5-9). The relative crystallinity of the materials was then calculated from the

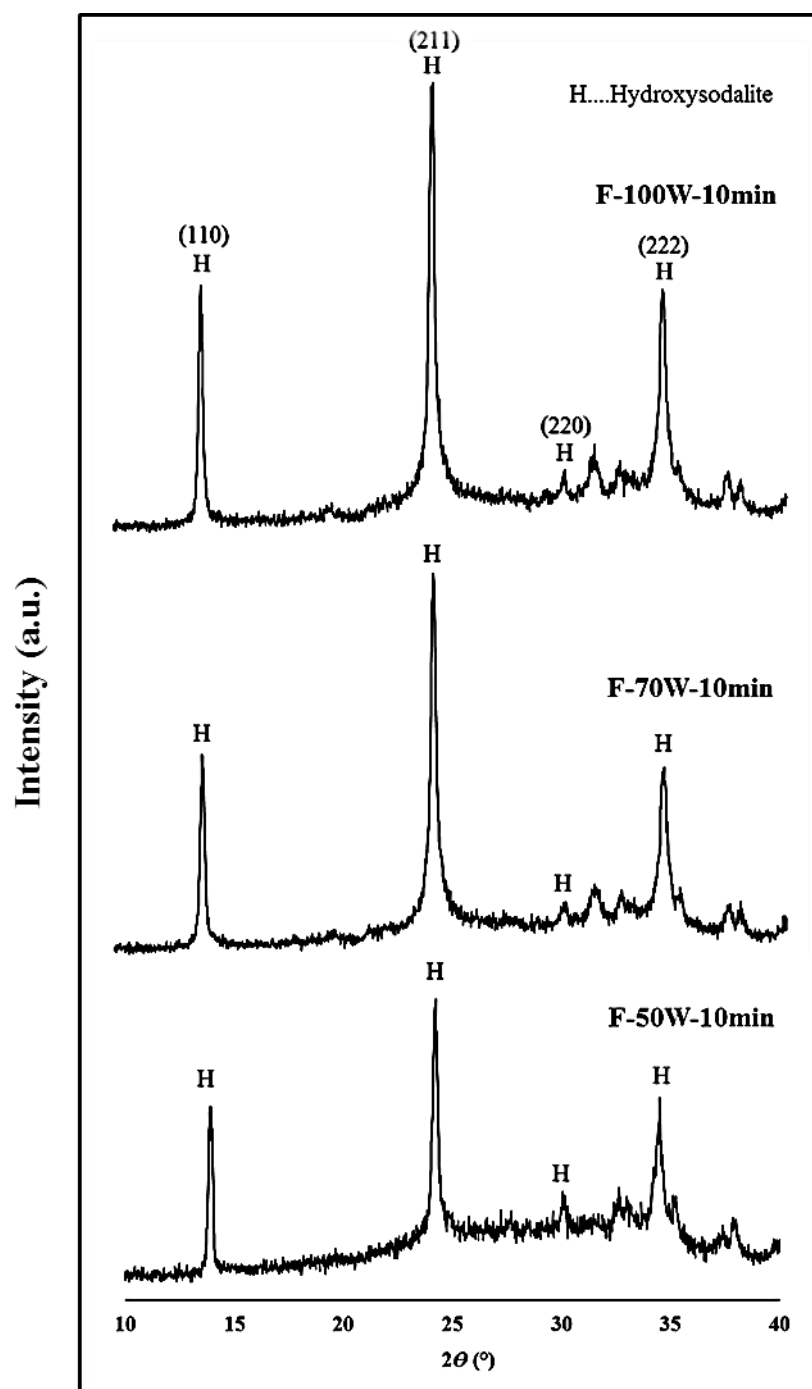


Figure 5-6. XRD patterns of the F-zeolites synthesized via MWCP mode

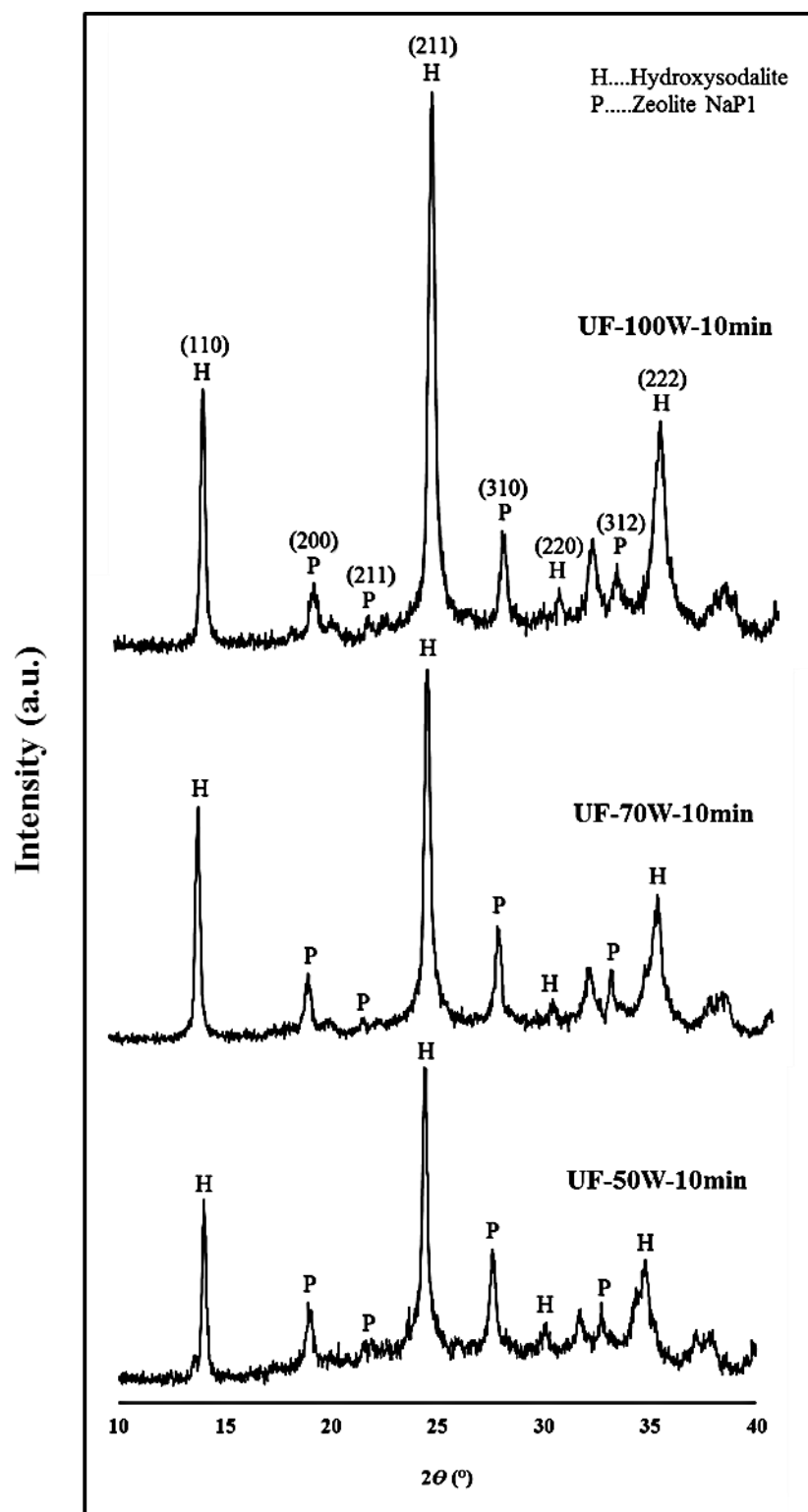


Figure 5-7. XRD patterns of the UF-zeolites synthesized via MWCP mode

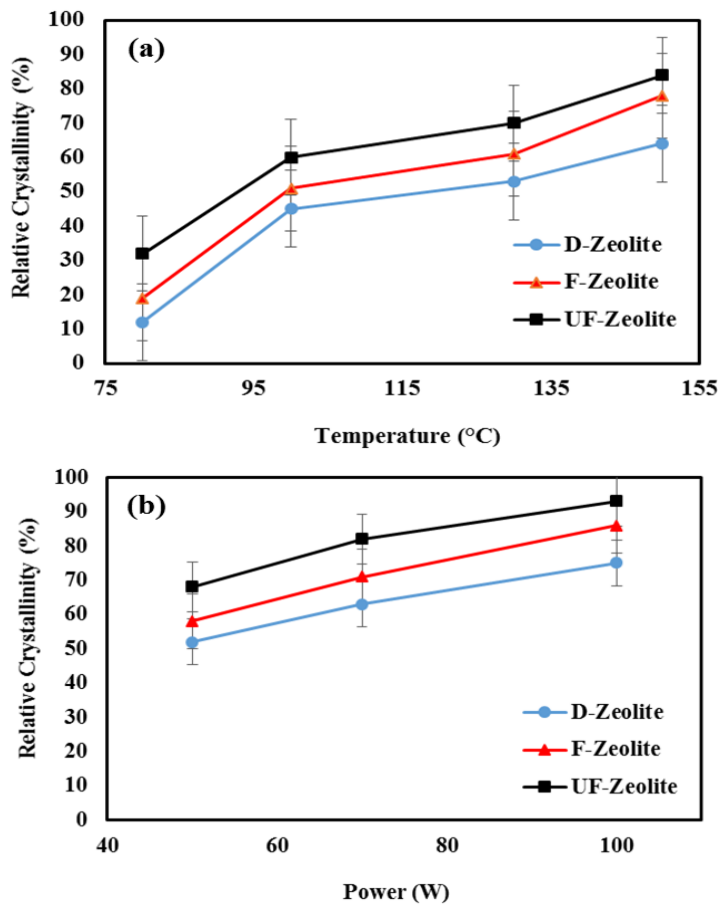


Figure 5-8. Relative crystallinity of D-, F-, and UF-zeolites as a function of (a) temperature and (b) radiation power

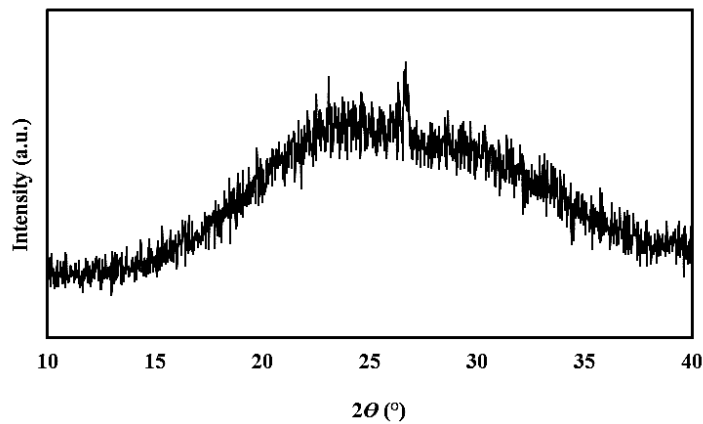


Figure 5-9. XRD pattern of the amorphous WG powder

relative amorphous phase percentages, as both are complementary values (Tarasi et al., 2013). The crystallinity of the zeolites increased with the elevation of temperature from 80 to 150°C and power

of radiation from 50 to 100W. It could be noticed from the trends that in both MWCT and MWCP modes (Figures 8a, b) UF-zeolites achieved supreme relative crystallinity. However, D-zeolites exhibited the lowest crystallinity over the whole range of temperature and radiation power. This demonstrates that the zeolites synthesized using leachate either by solid filtration or without filtration provided superior crystal growth efficiency as compared to the reference zeolite produced using DI water.

This could be justified by considering the difference between the ionic conductivity of leachate/DI water-based solutions and the way MW interacts with the available cations in these two cases. The presence of alkaline, alkaline earth (such as Na, K, Mg, and Ca) and heavy metals in the leachate could be mainly accredited to the leaching of some minerals from the landfill soil covers (Naveen et al., 2017; Kurniawan et al., 2006). The results of ICP analysis showed that the leachate used as the starting solvent contained elevated concentrations of Na (675.21 mg/L), K (163.40 mg/L), Ca (82.07 mg/L), and Mg (139.48 mg/L). The leachate source is also likely to contain other metals, which were not measured in this study. Therefore, leachate could provide various types of cations inside the reaction gel, while DI water (deionized) produce no cations. In another words, the ionic conductivity of leachate-based reaction gel could be higher than that of the DI water-based gel. This could be due to the lack of the cations' availability in DI water. As a result, MW and cations interaction could be more intensive in leachate solution leading to the generation of more hot spot zones in leachate-based gel compared to the DI water-based gel (Bukhari et al., 2015). More hot spot zones generated in leachate-based gel; therefore, promoted higher zeolite nucleation and crystallinity as compared to DI water-based gel.

According to Figures 5-8(a) and (b), the UF-zeolites also obtained superior crystallinity compared to F-zeolites. This indicates that the solid filtration after metal precipitation in leachate-based gel

could affect the crystallinity of the synthesized zeolites. The filtration of precipitated solids in filtered leachate reduced the concentration of the available cations inside the leachate-based gel and consequently the generation of hot spot zones. Therefore, greater nuclei formation and structural order occurred in the UF-zeolites gel than that of F-zeolites.

5.3.3. Phase ratio analysis

Figures 5-10(a) and (b) illustrate the trends of HS/NaP1 ratio versus temperature and radiation power for D-, F-, and UF-zeolites. A similar trend was observed for the HS/NaP1 phase evolution ratio for both MWCT and MWCP modes (as confirmed by XRD results). The fraction of HS over zeolite NaP1 increased as the temperature and power of radiation elevated in all D- and UF-zeolite samples. The generation of tiny hot spot zones, which is a consequence of increase in radiation power, favored the HS formation over zeolite NaP1. This indicates that generation of more hot spot zones create a more stable zeolitic phase (i.e. HS) and reduces the fractions of less stable phase like zeolite NaP1.

In both MWCT and MWCP cases, HS/NaP1 ratio was the highest for F-zeolites followed by D-zeolites. However, UF-zeolites had the lowest values over the entire ranges of temperature and radiation power. This demonstrates that the fraction of HS was lower in UF-zeolites due to the presence of comparable NaP1 fraction. However, more HS and less zeolite NaP1 fraction were observed in D-zeolites, while nearly no zeolite NaP1 was observed in F-zeolite. This trend could be attributed to the variation of Na^+ concentration in D-, F-, and UF-zeolite reaction mixtures after the metal precipitation and filtration pretreatments.

In leachate-based gels (i.e. F- and UF-zeolites), the Na^+ cation concentration originates from three sources: i) initial leachate, ii) WG precursor, and iii) NaOH that was added as the structure directing agent. However in DI water-based gel (i.e. D-zeolite), the Na^+ concentration could solely

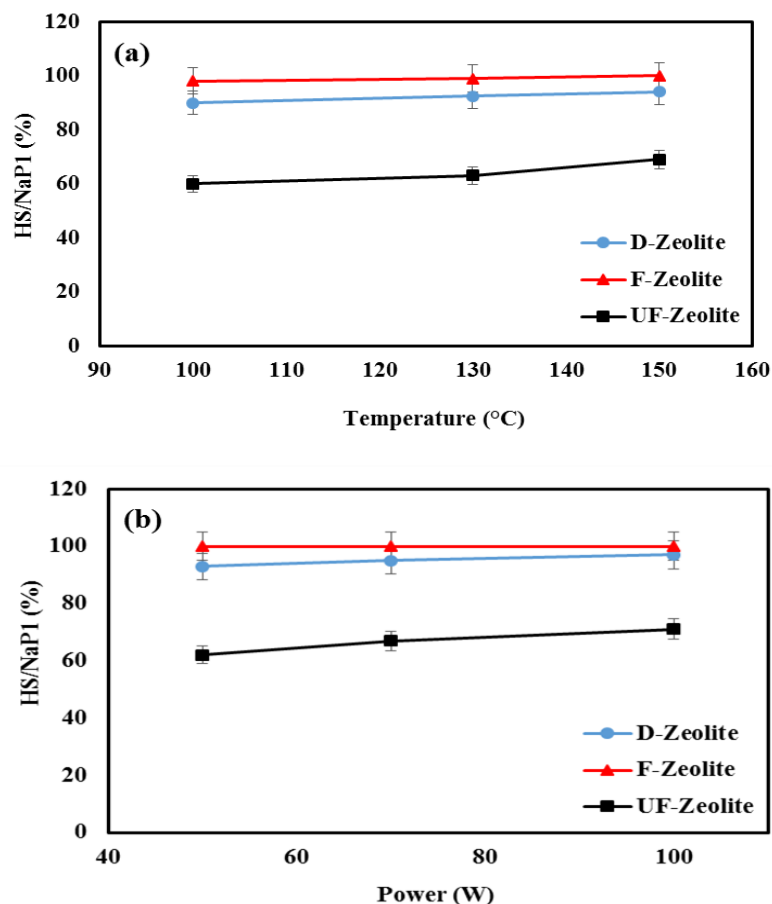


Figure 5-10. HS/NaP1 ratio of D-, F-, and UF-zeolites synthesized via (a) MWCT and (b) MWCP modes

come from the last two sources as the DI water may contain negligible amount of Na^+ . Therefore, the concentration of Na^+ in leachate-based gels like UF-zeolites without solid filtration could be potentially superior to DI water-based gels (D-zeolites). It is well known that the zeolitization process is strongly dependent on the interaction of alkali and alkali-earth cations like Na^+ with the negatively-charged soluble aluminosilicates to form a specific zeolite framework (Bukhari et al., 2015). Several previous reports have confirmed that more Na^+ concentration in the gel facilitates the formation of zeolite NaP1 and Chabazite (Murayama et al., 2002; Behin et al., 2014). This could be the main reason of the presence of small fractions of zeolite NaP1 in D-zeolites as compared to UF-zeolites. In the case of UF-zeolite, the considerable generation of hot spot zones

may have suppressed the large crystallization of zeolite NaP1. This has led to production of the major HS crystalline phase.

To provide a comparison between the leachate-based gels, the solid filtration after metal precipitation could have considerably reduced the Na^+ concentration in F-zeolite gel as compared to UF-zeolite without metal filtration. This substantial reduction of Na^+ concentration could be the main reason of roughly no zeolite NaP1 production (or roughly single-phase HS formation) in F-zeolites.

5.3.4. FTIR Results

FTIR spectroscopy is a worthwhile tool for obtaining the vibrational data to identify different functional groups in the materials. Therefore, spectra of WG as well as D-, F-, and UF-zeolites were collected and the results are shown in Figure 5-11. The FTIR spectrum of WG exhibits bands at 3475 cm^{-1} , 2358 cm^{-1} , 1646 cm^{-1} , 1024 cm^{-1} , 882 cm^{-1} , and 538 cm^{-1} . Based on the literature,

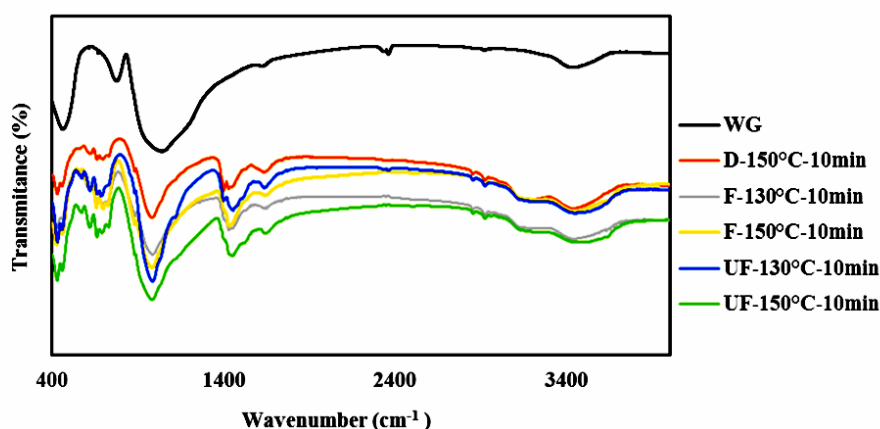


Figure 5-11. FTIR spectra of WG precursor as well as D-, F-, and UF-zeolites

the band centered at 3475 cm^{-1} signifies O-H molecule bending and stretching vibrational modes as well as the silanol hydrogen group Si-OH stretching mode within the glass framework (Naresh and Ham, 2016). The characteristic band observed at 2358 cm^{-1} corresponds to the O-H vibrational

modes generated at non-bridging oxygen locations (Naresh and Ham, 2016). The band observed at 1646 cm^{-1} could correspond to the vibrational modes of O-H group as well as Si-O bridging oxygen asymmetric stretching vibration formed inside the tetrahedral cells (Naresh and Ham, 2016). The couple of bands observed over the range of 1100 cm^{-1} - 500 cm^{-1} are attributed to the Si-O-Si vibrational mode in the matrix of SiO_4 tetrahedral structural cells (Kumar et al., 2010).

The FTIR spectra of D-, F-, and UF-zeolites also provided several characteristic bands at 450 - 1100 cm^{-1} , 1653 cm^{-1} , and 3475 cm^{-1} . The peaks at 1022 cm^{-1} correspond to the (Si, Al)-O asymmetric stretching internal vibration, those at 689 cm^{-1} correspond to the (Si, Al)-O symmetric stretching internal vibration, and peaks at 467 cm^{-1} correspond to the (Si, Al)-O bending internal vibration (Shoumkova and Stoyanova, 2013). The band attributed to O-H also became evident at about 1653 cm^{-1} (Sarria et al., 2006). A wide characteristic peak was also noticed at 3475 cm^{-1} , which was related to the O-H stretching vibrational mode formed in hydroxyl groups (Courtney et al., 2015). These results are consistent with the XRD phase identifications as the main zeolitic vibrational bands were observed on the IR spectra of the synthesized products. The characteristic band that appeared at 2358 cm^{-1} on the WG spectrum was not observed on the zeolite spectrum, indicating the conversion of glass into zeolite.

5.3.5. EDX Results

Figure 5-12 shows the EDX analytical composition results of the WG as well as D-, F-, and UF-zeolites. Elements including Al, Si, O, Na, Ca, K, and Mg were found in WG precursor and the synthesized zeolites. The WG provided a Si/Al ratio of roughly 13.3 indicating that the original glass source contained a high fraction of Si. This made it a suitable starting precursor for zeolite synthesis. The peak corresponding to C element in all EDX graphs is due to the use of the carbon

tape as the sample holder. The peak corresponding to Cu on the F-zeolite spectrum could be attributed to the incorporation of Cu that was originally available in the leachate into the sample.

The results showed that UF-zeolite gained a Si/Al ratio of roughly 0.66, while F- and D-zeolites obtained similar Si/Al ratios of 0.90 and 0.96, respectively. This indicates that the leachate-based zeolites, particularly UF-zeolites due to the least Si/Al ratio, could provide a superior ion exchange performance compared to the DI water-based zeolites.

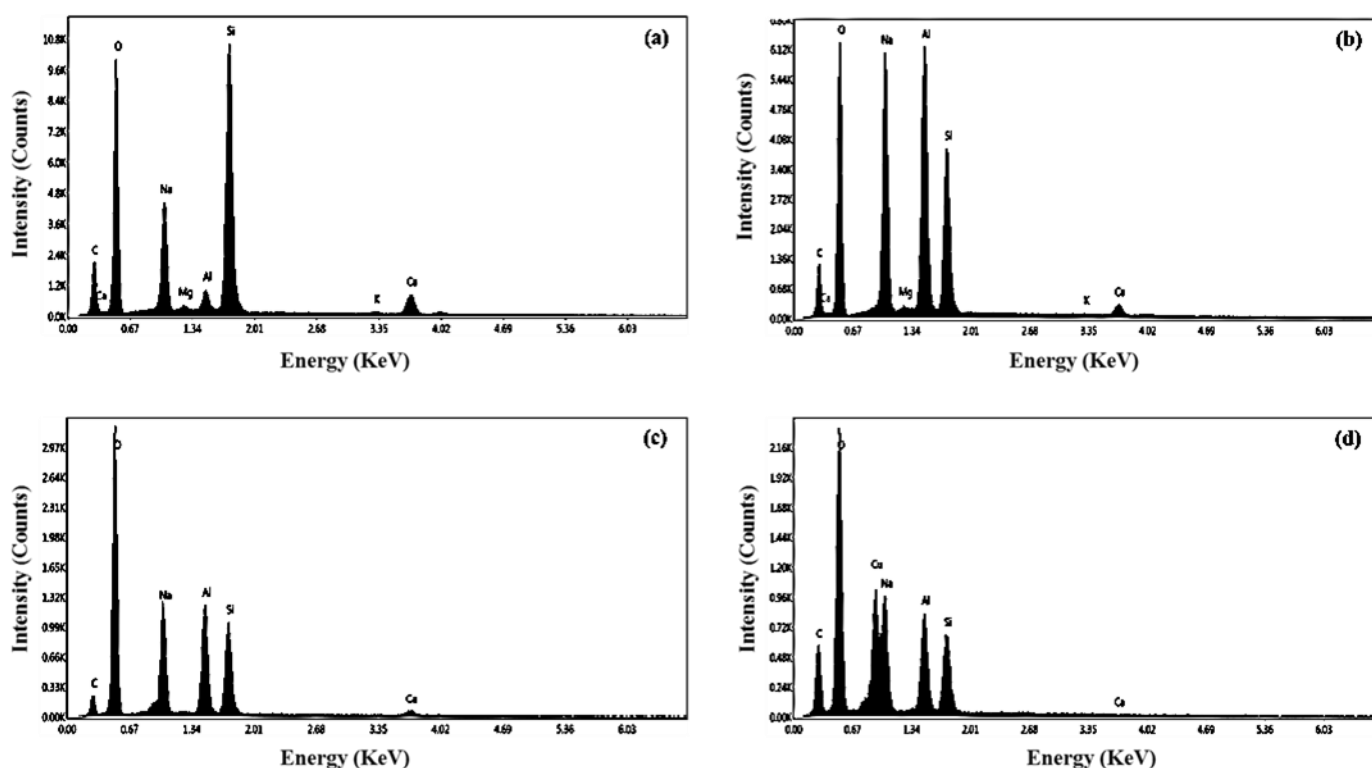


Figure 5-12. EDX elemental analysis of (a) WG cullet, (b) UF-zeolite, (c) D-zeolite, and (d) F-zeolite

5.3.6. SEM Results

SEM imaging was used in this study to provide information regarding the morphologies of the synthesized zeolites and to compare the crystal growth. Figure 5-13 shows the SEM images of the WG cullet as well as D-, F-, and UF-zeolites. The images illustrated in Figure 5-13 (b), (c), and (d) show the flower shape spheres and aggregated needle-like morphologies associated with HS

and zeolite NaP1, respectively (Esaifan et al., 2017). It was observed that the morphologies of zeolite crystals synthesized by leachate (F and UF-zeolites) were quite similar to the morphologies of DI water-based zeolites (D-zeolites). It was also observed that the spherical structures corresponding to HS are less noticeable in D-zeolite while they were abundantly available in F-zeolite. However, maximum accumulation of HS spherical and zeolite NaP1 needle-like morphologies was observed in UF-zeolite (Figure 5-13 (d)). These results are in agreement with the XRD phase analysis and confirm the superior crystal growth efficiency of UF-zeolite as compared to D- and F-zeolites (Figures 5-2 to 5-7).

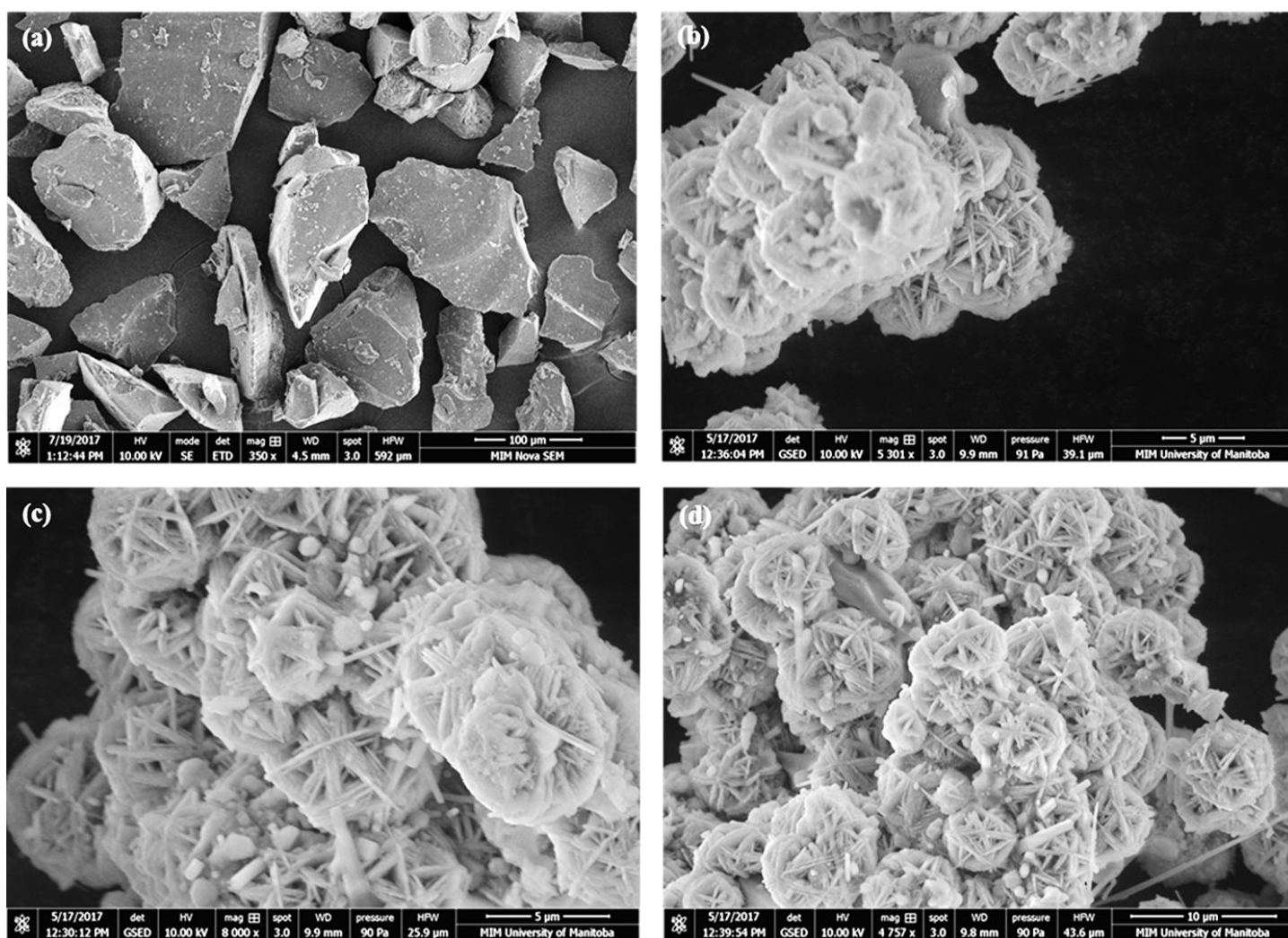


Figure 5-13. SEM images of (a) WG cullet, (b) D-zeolite, (c) F-zeolite, and (d) UF-zeolite

According to Figures 5-13 (b) to (d), it is theorized that the crystals' nucleation and growth occurred on the amorphous gel surface, which could also be deposited on the surface of glass particles. This agrees with the recent findings that zeolite crystallites are generated via a heterogeneous crystallization (Behin et al., 2014; Belviso et al., 2017).

5.3.7. TGA Results

The ability of a zeolite to adsorb water into its framework is an important trait. TGA results of the WG cullet as well as D-, F-, and UF-zeolites are shown in Figure 5-14. The results for the WG cullet show a very small weight loss (<1%) while the zeolitization strongly increased the weight loss potential. These results are assigned to the atmospheric moisture reversible sorption on the WG framework macropores and external surface. TGA data showed a maximum weight loss of 11.5% corresponding to UF-zeolite while F-zeolite and D-zeolite obtained lower values of 6.1% and 5.9%, respectively. The supreme weight loss of UF-zeolite compared to D- and F-zeolites is in agreement with EDX results as UF-zeolite obtained the least Si/Al ratio in the framework (more Al content in the framework results in more water sorption capacity). The close weight loss values of D- and F-zeolites is also congruent with the EDX results since both zeolite types obtained close Si/Al ratios in the framework. This trend is also visible in Figure 5-14(b) by considering the depth of the peaks resulting from the first derivation of the TGA curves at temperatures over 100°C. The deeper the peak, the greater is the amount of water adsorbed onto the micropores. The peak corresponding to UF-zeolite showed the largest depth while D- and F-zeolites corresponded to peaks with narrow depth. The maximum weight loss for the UF-, F-, and D-zeolites occurred at 138, 108, and 182°C, respectively (Figure 5-14b). These three points of inflection were observed due to the vaporization of the adsorbed moisture content available inside the capillary micropores of the obtained zeolites (Behin et al., 2014).

5.3.8. Cation Exchange Capacity (CEC) Results

The chemical activity of zeolites is mainly determined by the measurement of their CEC as it strongly depends on the Si/Al ratio of the framework. Figure 5-15 shows the CEC values of WG

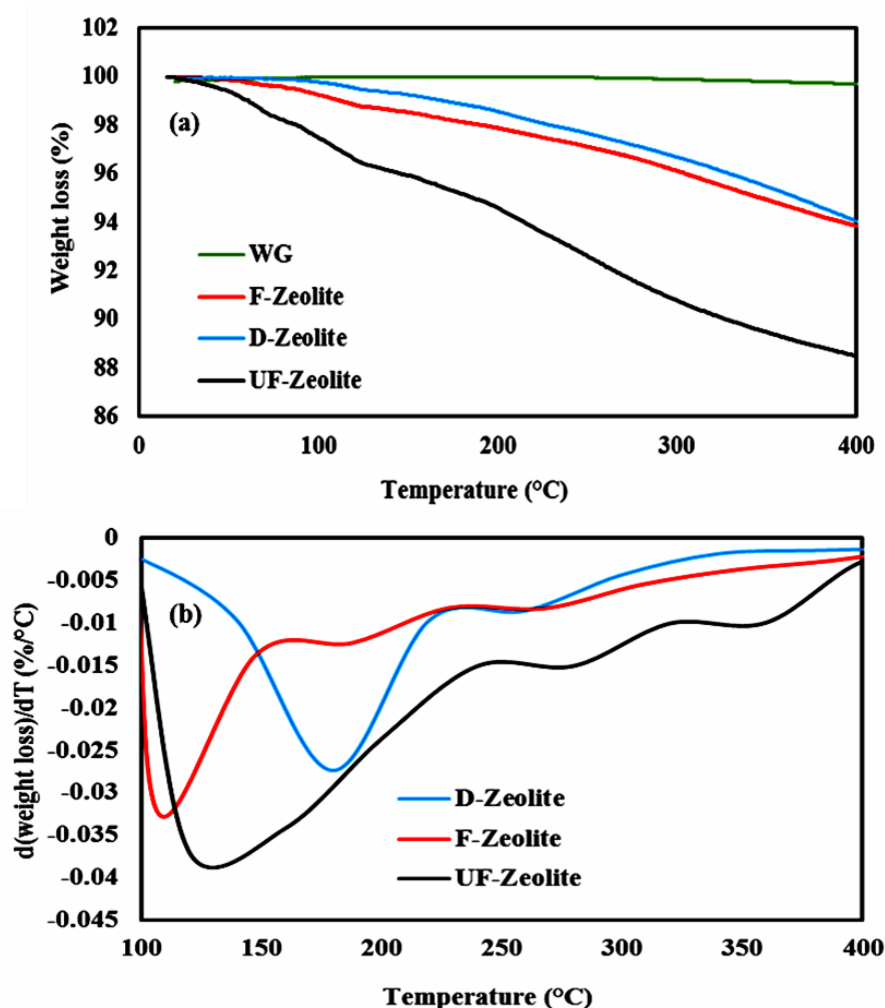


Figure 5-14. (a) TGA and (b) differential TGA of WG precursor as well as D-, F-, and UF-zeolites

as well as D-, F-, and UF-zeolites. The CEC value for the WG was 0.10 mol/g while UF-, F-, and D-zeolites obtained CEC values of 2.41, 1.35, and 1.29 mol/g, respectively. A higher value for UF-zeolite shows its superior ability for exchanging cations as compared to D- and F-zeolites. The largest CEC of UF-zeolite corroborates with the EDX results as UF-zeolite contained the maximum Al content (least Si/Al ratio) (Figure 5-12). The CEC of F-zeolite was numerically

higher than D-zeolite, but was quite close to that of D-zeolite. This is also in agreement with EDX results since the Si/Al ratio of both D- and F-zeolites had close values (Figure 5-12). The CEC value for UF-zeolite were also in congruence to the zeolites synthesized from coal fly ash (Kazemian et al., 2005; Belviso, 2017). This also shows that the UF-zeolite has a significant capability for a wide range of applications in various environmental remediation purposes as a useful ion exchanger.

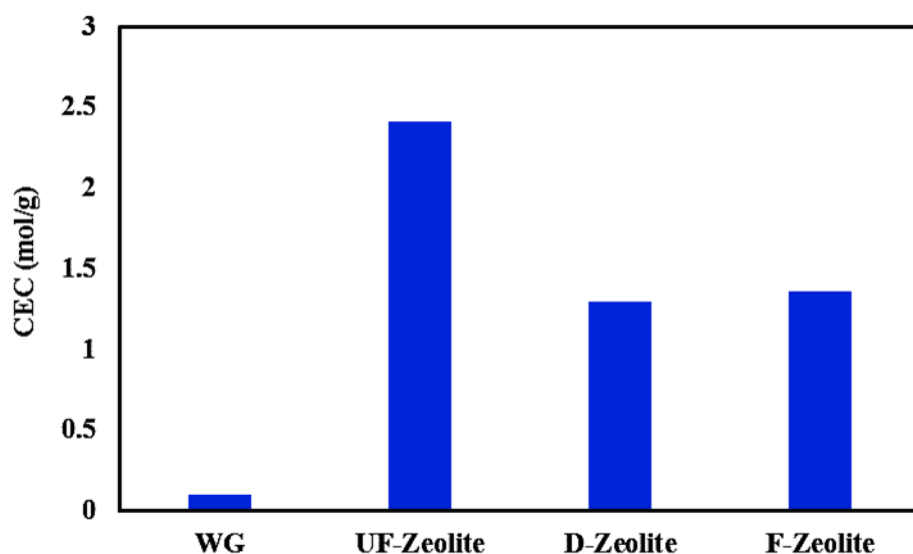


Figure 5-15. CEC values of WG precursor as well as D-, F-, and UF-zeolites

A brief comparison between the results obtained in this study and those reported by previous studies (used other alternative sources of water to synthesize zeolites) is represented in Table 5-1.

5.4. Conclusions

The study examined the microwave (MW) conversion of waste glass (WG) cullet into zeolite using landfill leachate as a novel solvent alternative. The zeolites were then compared with reference zeolites synthesized by DI water in terms of their characteristics (Si/Al ratio, water holding capacity, and CEC). The leachate-based gels were prepared in two sets of experiments, one with metal precipitation followed by filtration (F-zeolite), and the other with metal precipitation without

filtration (UF-zeolite). The DI water-based gel (D-zeolite) was prepared without metal precipitation and filtration pretreatments. The results showed that the zeolite synthesized by unfiltered leachate (UF-zeolite) provided a superior crystallinity as compared to D-zeolite. This

Table 5-1. Comparison between the results of previous studies used different sources of water for zeolite synthesis and results obtained in this study

References	Hydrothermal conditions				Zeolite	Type of (waste)water
	Method	NaOH (M)	T (°C)	t (h)		
Moreno et al. (2001)	CH	2.0	80-90	39	NaA, NaX	Etching bath residue from an Al-anodizing plant
Belviso et al. (2010)	CH	N.A.	35-90	96	NaA, NaX, HS	Seawater
Hussar et al. (2011)	CH	N.A.	75-95	1-3	NaA	By-products from aluminum etching process
Musyoka et al. (2011)	CH	N.A.	140	48	HS	Retentate effluent of a reverse osmosis mine water treatment plant
Musyoka et al. (2013)	CH	N.A.	140	48	NaP1, NaX	Circumneutral mine water
					HS	Acidic mine drainage water
Behin et al. (2014)	MW	N.A.	115-130	0.16-0.50	NaA	Wastewater of plasma electrolytic oxidation process
This study	MW	0.5	80-150	0.16	HS, NaP1	Landfill leachate

was attributed to the generation of more hot spot zones (and nucleation) in unfiltered leachate mixture due to the presence of metal cations other than Na^+ and the interaction of MW with gel cations.

Unfiltered leachate also generated the highest fraction of zeolite NaP1 while roughly no zeolite NaP1 was observed in F-zeolite. It was proposed that the solid filtration in filtered leachate substantially reduced the Na^+ concentration, and thereby suppressed the formation of zeolite NaP1. However, higher concentration of Na^+ in unfiltered leachate facilitated the formation of

comparable zeolite NaP1 fraction. DI water also produced much less fraction of zeolite NaP1 (and much more HS fraction) due to the lower Na^+ concentration compared to the unfiltered leachate. TGA and CEC results validated the EDX analysis confirming the least Si/Al ratio in UF-zeolite. This demonstrated the higher ability of exchanging cations and water holding capacity of UF-zeolite, which makes it suitable for a broadened range of applications including environmental remediation purposes.

Chapter 6. Synthesis of Al-substituted 11Å tobermorite using waste glass cullet: A study on the microstructure *

Type of experiment	Scientific contribution
Conventional heating synthesis	A.R. Majdinasab conducted all the synthesis experiments using conventional heating technique.
XRD	A.R. Majdinasab prepared the samples and did the data collection.
EDX	A.R. Majdinasab prepared the samples and A. Khan from the Manitoba Institute of Materials (MIM) did the data collection.
SEM	A.R. Majdinasab prepared the samples and A. Khan from the Manitoba Institute of Materials (MIM) did the data collection.
FTIR	A.R. Majdinasab prepared the samples and did the data collection.
DSC	A.R. Majdinasab prepared the samples and A. Soleiman from the IKO Materilas Testing Facility at the Civil Engineering Department did the data collection.
NMR	A.R. Majdinasab prepared the samples and S. Kroeker from the Chemistry Department did the data collection.

*This chapter has been published as: Majdinasab, A., & Yuan, Q. (2020). Synthesis of Al-substituted 11Å tobermorite using waste glass cullet: A study on the microstructure. *Materials Chemistry and Physics*, 123069.

This chapter was fulfilled with the main objective of synthesizing well crystalline 11Å tobermorite using waste glass precursor with a focus on the microstructure and to detect the type of synthesized tobermorite whether it is Al substituted. This chapter contributed to the main objectives by suggesting the best synthesis parameters at which a well crystalline pure 11Å tobermorite could be synthesized and could be hydrothermally stable. The results obtained in this chapter further contributed to the objectives as they showed that the 11Å tobermorite synthesized using waste glass cullet was Al substituted and the Al substitution was preferentially occurred at bridging and branching sites within the silica polymerized chains that improves the polymerization degree of the chains.

Abstract

Calcium silicate hydrate (CSH), the key by-product of Portland cement hydration, due to the structural resemblance, is mainly represented as a defect tobermorite analog. To provide an extensive overview on the impact of Al incorporation in CSH, synthesis of Al-substituted 11 Å tobermorite using waste glass cullet (WGC) was investigated and compared with an Al-free reference. The optimal parameters of 180°C curing temperature, 5h curing time, 0.5M of activator concentration, and Ca/Si of 0.83 were found via XRD to synthesize pure crystalline tobermorite. SEM micrographs also showed that Al incorporation changed the tobermorite morphology from platy-like shape to acicular crystals. The WGC synthesized tobermorite exhibited similar thermal behavior to reference tobermorite as observed via DSC such as the free water release at 55°C, interlayer water release at 131°C, Si-O-H bond cleavage at 680°C, and recrystallization to wollastonite at 820°C. ^{29}Si and ^{27}Al NMR analysis showed that Al substitution preferably occurred at bridging (Q^2) and branching (Q^3) positions. The results from this study could significantly contribute to the application of Al-based wastes in concrete and mortar construction to improve the microstructure of the hydration by-products.

6.1. Introduction

Tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) is a calcium silicate hydrate (CSH) that naturally occurs at hyper-alkaline geothermal conditions. Its crystalline structure was first studied by Heddle at Tobermory, Scotland in 1880 (Heddle, 1880; Megaw and Kelsey, 1956). Tobermorite is well-known primarily as a structural analog of the major phase of hydrated cement paste due to the structural resemblance. In 1953, Tylor et al. (1953) claimed that highly-crystalline CSH type I could be fundamentally identical to tobermorite in terms of the microstructure. Tobermorite is available as the main phase in most building materials such as fiber-reinforced calcium silicate sheets, thermal insulation boards, sand-lime bricks, and autoclaved aerated concrete (Claringbull and Hey, 1952; Maeshima et al., 2013).

The mechanical properties including durability of concrete is mainly evaluated by the presence of CSH in the hydrated cement paste, as this phase highly contributes to the concrete's performance. Recently, lots of research has been focused towards the production and analysis of the CSH microstructure. However, a fully detailed structural analysis of CSH is lacking due to its complex microstructure (Lothenbach and Nonat, 2015; Gartner and Maruyama, 2017). The properties and microstructure of the family of this mineral vary locally; therefore, it is referred as a "gel". On the other hand, hydration of cement is a complicated phenomenon resulting in a broad range of species with a variety of properties (Land and Stephan, 2015; Marchon and Flatt, 2016). As a result, CSH would not exist as a single phase in a regular hydrated cement paste; therefore, its direct detection is a difficult task. Concrete has an intricate heterogeneous microstructure, ranging from nanopores for paste to micropores for aggregates. This complicated heterogeneous matrix makes it challenging to probe the contribution made by each individual component to the overall macroscopic properties (Morshedifard et al., 1785; Qomi et al., 2018).

CSH exhibits a layered microstructure, which is quite similar to that of the ideal crystalline tobermorite layered structure. Therefore, tobermorite has been considered as an important structural analog to analyze CSH microstructure (Feldman and Beaudoin, 1976). CSH microstructure could be simply defined as a defect tobermorite microstructure with a central calcium oxide layer clamped on both sides by infinite silica chains arranged in a “dreierketten” structure (Maeshima et al., 2003; Blanc et al., 2010). In this arrangement, the repeating chains of three silica tetrahedral consisting of two pairing tetrahedral sharing their oxygen atoms with the central calcium oxide sheet. A third bridging tetrahedron joins the isolated pairing dimers to develop indefinite polymerized silica chains. Numerous layers are linked together with an interlayer space containing calcium, alkalis, aluminum, and water (Puertas et al., 2011; Lodeiro et al., 2009; Stark, 2011; Kulik, 2011).

The significant interest in investigating tobermorite is due to its structural similarity to the CSH minerals that are produced during Portland cement hydration. In hydrated cement paste, most of the produced CSH phases suffer from the lack of high structural order thereby making it difficult to characterize by means of X-ray diffraction or electron microscope techniques. Hence, there is a lack of understanding pertaining to CSH microstructure (Jennings, 2000; Jennings, 2008; Petersen et al., 2018; Monasterio et al., 2015). Over the recent years, significant attention has been paid to the production of synthetic tobermorite using various kinds of industrial waste by-products with the focus on the crystalline structure of tobermorite. Various parameters such as prolonged synthesis times (generally several days) as well as elevated temperatures pose as the main challenges of synthesizing tobermorite structures using these wastes. Therefore, application of mineral alkali activators has been suggested to accelerate the transformation (Jing et al., 2007; Nakahira et al., 2008). These wastes include trachyte rock, blast furnace slag, fly ash, newsprint recycling residue, and municipal incineration bottom ash (Jing et al., 2007; Nakahira et al., 2008;

Youssef et al., 2010; Coleman et al., 2003). Moreover, utilization of waste glass cullet as the starting feedstock to produce synthetic tobermorite to characterize the microstructure requires further investigation.

Based on a report published by the US Environmental Protection Agency, approximately 10.37 million tons of waste glass (WG) was produced in the US in 2013; out of which, only 2.78 million tons was recycled. This resulted in the disposal of 7.59 million tons of waste glass cullet (WGC) in the landfills (USEPA, 2015). European Union nations in the same year produced a total of 1.5 million tons of WGC with the approximate recycling rate of 79% (Triguero et al., 2016). Although the recovery rate of WGC may be significant, only a tiny fraction of this amount could be co-melted with natural sources for the remanufacturing of glass. Generally, glass is collected and separated by color. Mixed-color WG is not recyclable due to the problems associated with the chemical mismatch and variations in the melting temperature for different glass types (Ashuri et al., 2012; Hamedani et al., 2011), which has resulted in a large mass of discarded WGC in landfills each year. To address this environmental issue, novel strategies should be implemented to upcycle extra WGC into the synthesis of value-added products such as tobermorite. Apart from being the main binder in the hydrated cement paste, tobermorite has other potential applications in wastewater treatment such as an adsorbent and an ion-exchanger as well as a thermal insulant in building materials (Shrivastava and Shrivastava, 2000; Bai et al., 2015).

Due to the presence of soluble alumina in the concrete pore solution as a result of cement hydration, studying the mechanism of aluminum (Al) interaction with CSH binder is of great importance. Many research studies notified that Al could be substituted at Q^2 and Q^3 sites in the silica chains to form Al-substituted CSH (Guo et al., 2017; Wang et al., 2017). In these studies, Q is a single silica tetrahedron connected to two or three other silica sites to form the polymerized silica chains

within CSH microstructure (Maeda et al., 2011). One of the studies utilized an in-situ time-resolved X-ray diffraction method to study the effect of Al addition on tobermorite formation (Matsui et al., 2011). They found that the structure of initial CSH phase is important for the consequent tobermorite formation, and the tobermorite synthesis accelerated with the addition of Al. In another study, Al availability retarded the initial formation of CSH by decreasing the solubility of silica, but accelerated synthesis of tobermorite at later ages (Shaw et al., 2000). However, these phenomena occurring during cement hydration are too complicated, and the mechanism of the Al incorporation within the CSH gel as well as the properties of Al-substituted tobermorite need further investigation.

The main objective of this study is to investigate the synthesis and microstructure of 11 Å tobermorite with and without the presence of Al using WGC as the source of Si and Al. The influence of Al substitution (from the WGC precursor) on the microstructure of tobermorite was probed by means of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), magic angle spinning nuclear magnetic resonance (MAS-NMR), energy dispersive X-ray spectrometer (EDX), Scanning electron microscope (SEM), and differential scanning calorimeter (DSC). The effect of other parameters including temperature, reaction time, alkali activator concentration, and Ca/Si on the purity and crystallinity of the synthesized tobermorite was also examined. The current study could provide a better understanding of the role of Al incorporation in the cement paste binder on the atomic scale and the macroscopic behavior of the concrete.

6.2. Materials and Methods

6.2.1. Materials

WGC was collected from the recycling plant of Manitoba Liquor and Lotteries (Manitoba, Canada). A 30-mesh sieve (0.595 mm) was used to sieve the WGC at the initial stage. To increase

the surface-to-volume ratio of the sieved particles, the powder was then pulverized using a Laboratory Mill (MINICER NETZSCH, Germany). The pulverization conducted at 400rpm for 40min after the addition of 10g of the sieved WGC and 200 mL of deionized (DI) water to the bowl containing ZrO_2 spherical beads with 30-mm diameter. To separate the solid phase, the suspension was left at room temperature for 12h and the liquid residue was removed. The settled WG powder then dried in an oven for 24 h at 70°C , and then ground to a well-separated and uniform powder using mortar and pestle. Analytical grade calcium oxide (CaO , 99%; Sigma-Aldrich, USA), sodium hydroxide (NaOH ; Sigma-Aldrich, USA), and fumed silica (SiO_2 , 0.007 μm , Sigma-Aldrich, USA) were utilized as-received. Deionized (DI) water was used as a media for the preparation of the solutions prior to the hydrothermal reactions.

6.2.2. Synthesis procedure

All synthetic tobermorite specimens were prepared by mixing the WGC and the aforementioned chemicals via a hydrothermal reaction as follows. In the first step, the Ca/Si ratio of the mixtures was adjusted at 0.83, based on the composition of the ideal tobermorite ($\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16}\cdot 4\text{H}_2\text{O}$). In all batches, the water/solid ratio of the solutions was maintained constant at 10.00. The solutions were stirred for 20 min at room temperature, then transferred to a 45 mL autoclave stainless steel vessel, and finally placed in an oven to undergo hydrothermal reactions. The samples were then filtered and washed thrice with DI water. Samples were oven-dried at 70°C for 24 h and ground with mortar and pestle prior to further characterization.

In this study, the key parameters that affect the phase purity and crystallinity of synthesized tobermorite using WGC including reaction time, reaction temperature, alkali activator concentration, and Ca/Si ratio were investigated. Analytical grade sodium hydroxide (NaOH) was used as an alkali activator in this study. The aforementioned parameters were optimized by varying

one of the parameters and keeping the other ones constant over the synthesis duration. The overall synthesis conditions for the conversion of WGC to Al-substituted 11 Å tobermorite is summarized in Table 6-1. WGC is used as the main precursor for Si and Al. The elemental composition of the WGC obtained by EDX analysis is presented in Figure 6-1. The WGC precursor exhibited an Al/Si ratio of roughly 0.07 (Figure 6-1), which is a suitable value for a starting gel to synthesize Al-substituted 11 Å tobermorite, according to the results reported by several other studies (Guo et al., 2017; Wang et al., 2017). The sample with the optimal properties in terms of the tobermorite

Table 6-1. Ranges and values of the experimental parameters for tobermorite synthesis using WGC

Experimental set	Reaction time (h)	Activator concentration (M)	Temperature (°C)	Ca/Si	Water/solid
1	2-72	0.5	180	0.83	10.00
2	5*	0.5-4	180	0.83	10.00
3	5*	0.5*	120-200	0.83	10.00
4	5*	0.5*	180*	0.83-2.00	10.00

* refers to suitable parameters' values selected from previous set to be applied for the next sets of experiments.

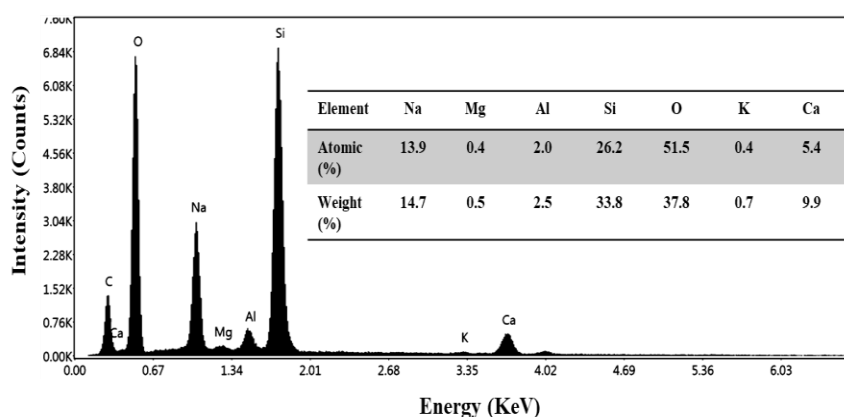


Figure 6-1. Elemental composition of the WGC precursor obtained via EDX analysis

crystallinity and purity was selected from the set of experiments conducted using WGC as presented in Table 6-1 (with Al). This sample was compared with a reference sample synthesized using a CaO-SiO₂-H₂O system (without Al) under the same experimental conditions. Analytical grade fumed silica used as a Si source for the synthesis of reference tobermorite. The samples were compared and characterized by means of XRD, ²⁹Si NMR, EDX, FTIR, and DSC to investigate the effect of Al substitution on the microstructure of tobermorite-like CSH microstructures.

6.2.3. Characterization techniques

Characterization of the samples was done using various analytical techniques. The samples were placed on a zero-background quartz slide to detect the crystalline phases over the range of $5^{\circ} < 2\theta < 60^{\circ}$ using a D8 ADVANCE Bruker diffractometer with CuK_α (average $\lambda = 1.5418 \text{ \AA}$) at room temperature (40 kV with 0.02° step size). The 1-mm hole on the slide adjusted the zero background of all samples by normalizing all the specimens. DIFFRAC.SUITE EVA software was used to conduct the phase matching analysis and the suitable phase options were selected. Reference patterns exist in the crystallographic sources as well as the literature data were also used to corroborate with the obtained results (Guo et al., 2017; Matsui et al., 2011).

A Scanning electron microscope (SEM) (JSM-6701F, Hitachi, Japan) with accelerating voltage of 10 kV was used to detect the crystals morphology. An energy dispersive X-ray spectrometer (EDX) (JSM-6701F, Hitachi, Japan) was used to analyze the elemental composition of the WGC precursor and synthesized samples. The collection of the specimens Fourier transform infrared (FTIR) spectra was done by pelleting the sample powders with KBr over the scan range of 400-4000 cm⁻¹ using a Spectrometer (GX FTIR, Perkin Elmer Spectrum , USA). A thermal analyzer (TGA-DSC SDT Q600 V20.9 Build 20, TA Instruments, USA) was used to evaluate the thermal

behavior of the specimens. A nitrogen gas flow was purged and the specimens were heated at the rate of 10°C/min over the temperature range of 30°C to 1000°C.

The local atomic structure was characterized by solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR). The ^{29}Si MAS-NMR spectra was collected using a spectrometer (Bruker AVANCE III 400 MHz, 9.4T, Fallanden, Switzerland) operated at 79.4 MHz. Chemagnetic probe of 4 mm was used at the spin rate of 8.0 kHz. Tetramethylsilane was used as a reference for relative measurements of the chemical shifts. The spectra were recorded in direct polarization with decoupling of ^1H , 10.2 ms of acquisition time, and 30 s of recycle delay. Each specimen was scanned 2800 times on average. The ^{27}Al MAS-NMR spectra were also recorded via the same spectrometer operated at 10.40 MHz. The instrument used a 4 mm MAS probe at 12.0 KHz spin rate. The relative measurement of chemical shifts was done using aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) as a reference. The delay of recycle was 5 s and the angle of flip was adjusted at $\pi/12$. Each sample was scanned 1024 times with an acquisition time of 5.1 ms.

6.3. Results and discussion

6.3.1. XRD analysis

6.3.1.1. Effect of reaction time

To study the effect of reaction time on the structure of the tobermorite specimens, the first set of experiments was conducted with varying reaction time between 2~72h. Figure 6-2 presents the XRD patterns of the specimens synthesized at the aforementioned reaction time range obtained at 180°C, Ca/Si of 0.83, and activator (NaOH) concentration of 0.5M. The type of tobermorite microstructure could be determined by tracking the position of (002) reflections at 2θ angles lower than 10° in the XRD patterns (Maeshima et al., 2003). The 14°Å , 11°Å , and 9°Å tobermorite structures are represented by the (002) reflections positioned at 2θ values of around 6° , 8° , and

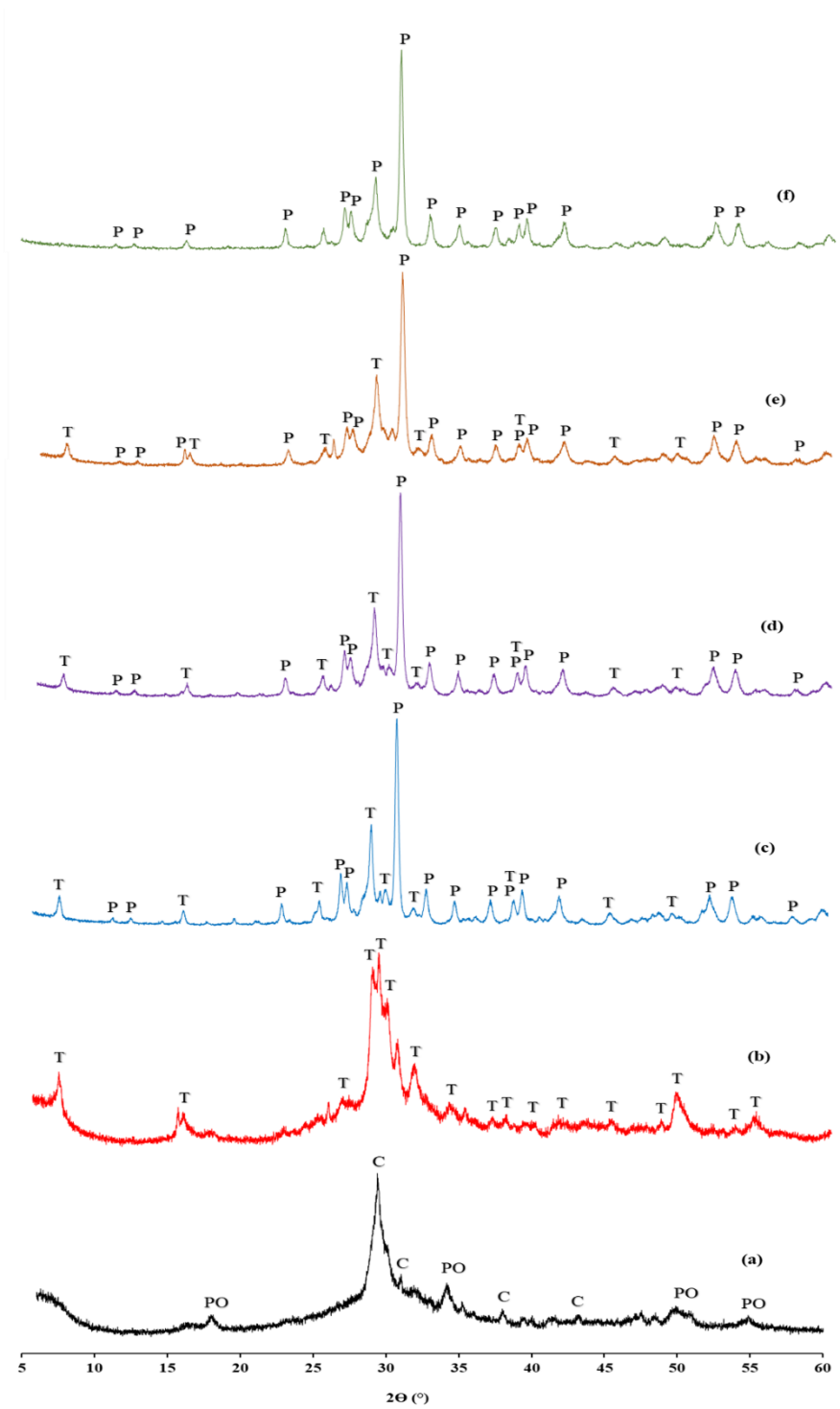


Figure 6-2. XRD patterns of the samples synthesized at 180°C, Ca/Si= 0.83, and activator concentration of 0.5M for (a) 2h, (b) 5h, (c) 10h, (d) 24h, (e) 48h, and (f) 72h. Note: T- Tobermorite; PO-Portlandite; C-Calcite; P-Pectolite.

10°, respectively. Several studies have highlighted the significance of reaction time on the tobermorite structure and formation (Nakahira et al., 2008; Guo et al., 2017). According to Figure 2, poorly crystallized structure was observed at 2h of reaction time with no characteristic peaks related to the tobermorite structure. In this case, the main phases of portlandite ($\text{Ca}(\text{OH})_2$) (PDF card number 00-087-0673) and calcite (CaCO_3) (PDF card number 050586) were observed. This indicates that part of the free Ca^{2+} in the solution has been carbonated instead of reacting with amorphous SiO_2 due to the short reaction time, while the remaining free Ca^{2+} retained in the form of portlandite.

At 5h of reaction time, the roughly pure single-phase 11 Å tobermorite (PDF card number 01-083-1520) was synthesized with the main characteristic reflections of (002), (110), and (200) observed at 2θ values of 8.01°, 29.56°, and 31.06°, respectively. The pattern of the sample synthesized at 5h reaction time showed no peaks representing residual portlandite or calcite. This shows that higher reaction time of 5h was marginally better for the free Ca^{2+} and soluble amorphous SiO_2 to react and form pure 11 Å tobermorite phase without any other impurities. As the reaction time increased to 10h, a decrease in the (002) peak intensity at around 8° 2θ representing 11 Å tobermorite occurred and a strong reflection at 31.43° characteristic of pectolite (PDF card number 00-033-1223) phase was detected. The same trend was also observed as the reaction time further increased to 24 and 48h. This is mainly due to the unstable structure of tobermorite-like CSHs showing greater affinity to transit into more stable structures such as pectolite at prolonged reaction times. This effect was further pronounced at the reaction time of 72h. In this case, the characteristic peaks of 11 Å tobermorite disappeared and pure pectolite phase was obtained. Based on the above results, 5h was revealed as an optimal reaction time and was applied to the next sets of experiments to investigate the effect of other synthesis parameters.

6.3.1.2. Effect of alkali activator concentration

To study the effect of alkali activator concentration on the formation of 11 Å tobermorite, the second set of experiments was conducted with varying NaOH concentrations between 0.5~4.0M.

Figure 6-3 presents the XRD patterns of the samples synthesized at the aforementioned NaOH

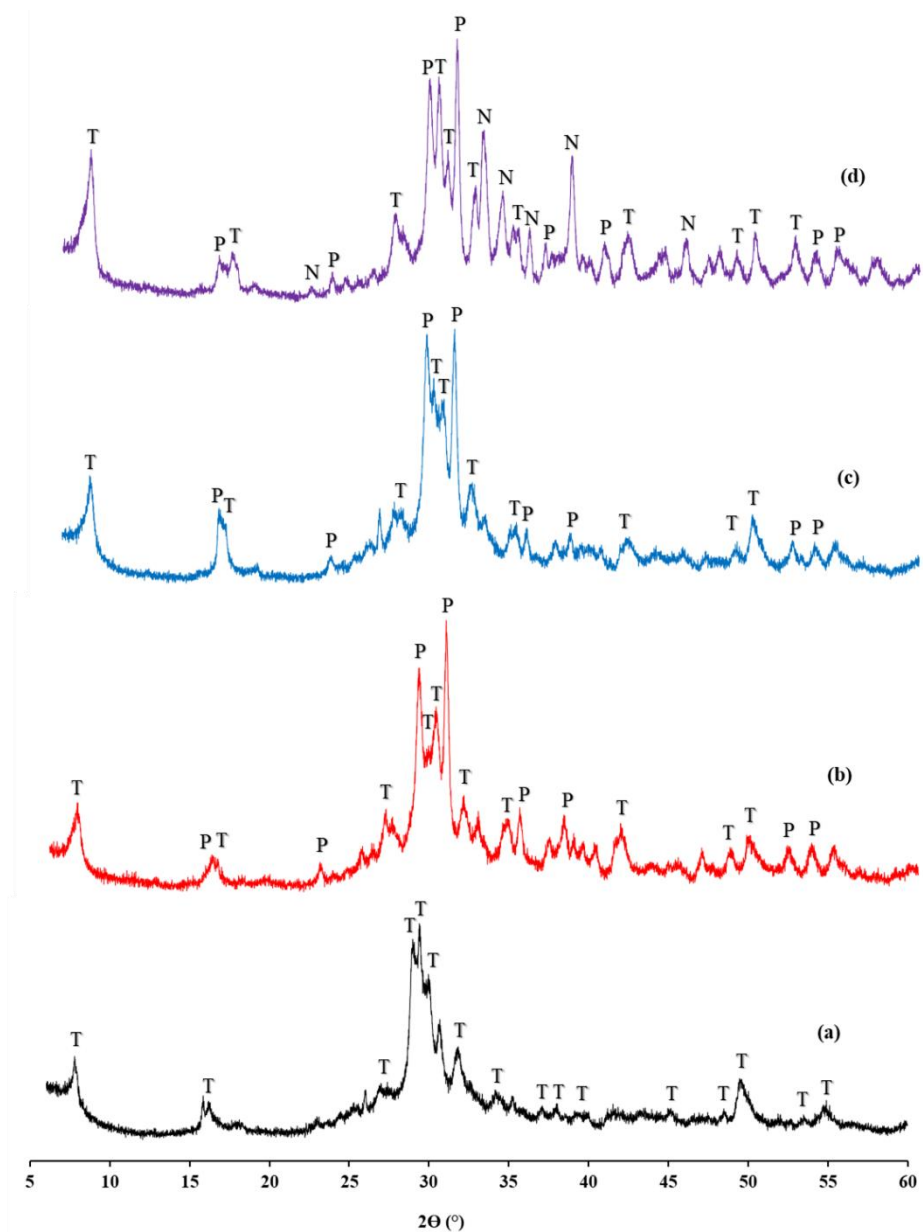


Figure 6-3. XRD patterns of the samples synthesized at 180°C, Ca/Si= 0.83 for 5h at activator concentrations of (a) 0.5M, (b) 1.0M, (c) 2.0M, and (d) 4.0M. Note: T- Tobermorite; P-Pectolite; N- Na₂CO₃

concentration ranges at 180°C, Ca/Si of 0.83, and 5h of reaction time. At 0.5M of activator concentration, pure 11 Å tobermorite was obtained with the characteristic (002) reflection observed at around 8° 2 θ . With the increase to 1.0M, strong peaks characteristic of pectolite phase were observed at 2 θ values of 28.68° and 31.06°. The same trend was also observed at the activator concentration of 2.0M. In this case, the XRD pattern demonstrated stronger characteristic reflection of pectolite at 28.68° and consequently yielded more pectolite phase. This is also in agreement with Liu et al. (2013), which reported that Na⁺ concentration has a remarkable impact on the morphology, microstructure, and composition of the tobermorite-like CSHs. At high Na⁺ concentration, the tobermorite-like CSH structure can transit into pectolite. Therefore, to produce pure synthetic CSHs with defect tobermorite structures, it is essential to monitor Na₂O content in the CaO-SiO₂-H₂O system (Liu et al., 2013). Further increasing the activator concentration to 4.0M resulted in the formation of a third sodium carbonate (Na₂CO₃) phase (PDF card number 00-045-1479). This could be attributed to the carbonation of extra Na⁺ in the solution not taken up by either the CSH or the pectolite structures. Consequently, remaining Na⁺ formed a separate Na₂CO₃ phase. Pectolite was still detected as a major crystalline phase at 4.0M of activator concentration. Therefore, 0.5M was found as a suitable activator concentration for the synthesis of 11 Å tobermorite. This value was used to conduct further experiments to examine the effects of reaction temperature and Ca/Si.

6.3.1.3. Effect of reaction temperature

Several studies have pointed out that the reaction temperature has a strong impact on the nucleation and crystal growth of the CSH structures (Zou et al., 2016; Zou et al., 2018). Therefore, a range of temperature between 120-200°C was investigated for the synthesis of 11 Å tobermorite. The XRD patterns of the samples synthesized with the reaction temperatures within the aforementioned

range and Ca/Si of 0.83 for 5h of reaction time and 0.5M of activator concentration are shown in Figure 6-4. At 120°C and 150°C, no diffractions characteristic of 11 Å tobermorite were observed and the samples were mainly a combination of portlandite and calcite phases. However, roughly pure single-phase 11 Å tobermorite synthesized at 180°C with the main (002) characteristic peak was detected at around 8° 2 θ . These results indicated that temperatures less than 180°C does not

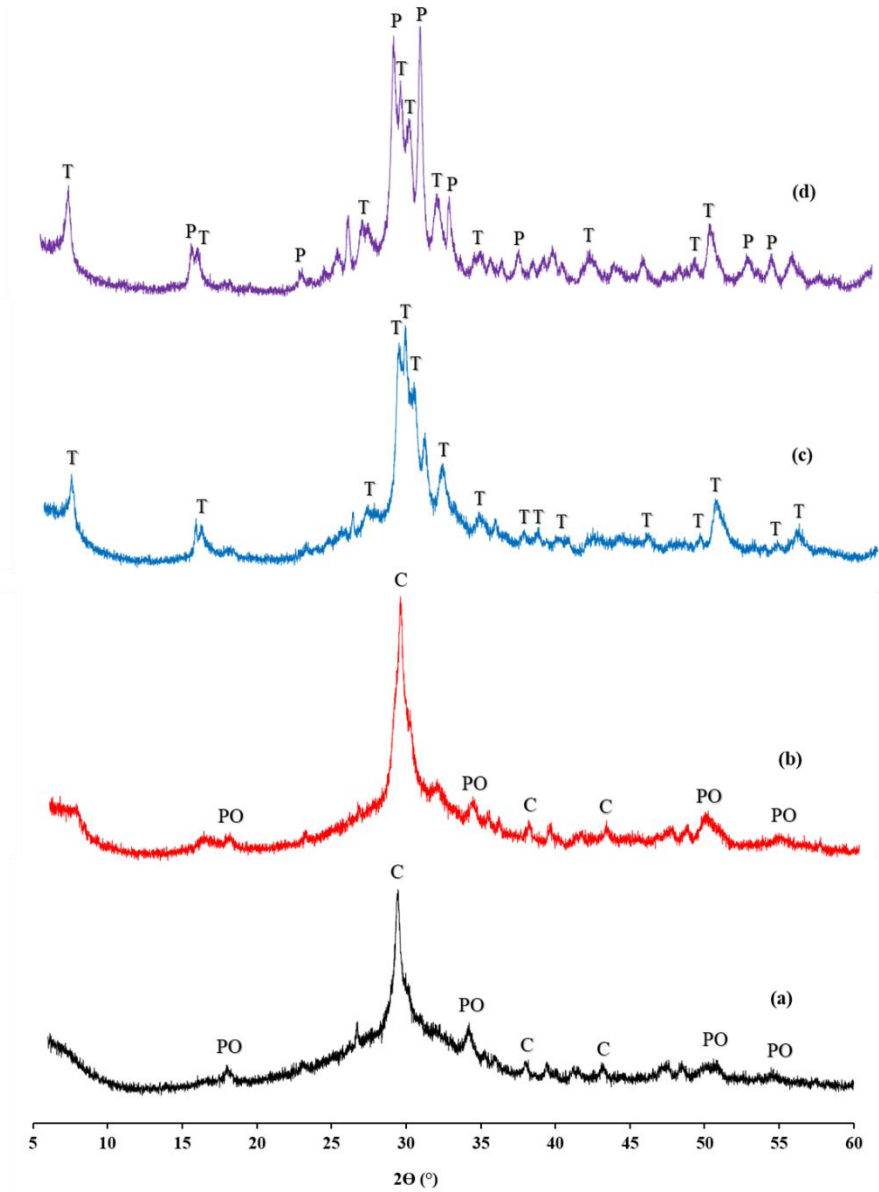


Figure 6-4. XRD patterns of the samples synthesized at Ca/Si= 0.83 for 5h and activator concentration of 0.5 M obtained at (a) 120°C, (b) 150°C, (c) 180°C, and (d) 200°C. Note: T- Tobermorite; PO-Portlandite; P-Pectolite; C-Calcite.

meet the energy demand for the completion of the polymerization reaction. As a result, most of the free Ca^{2+} in the solution remains either unreacted in the form of portlandite or becomes carbonated to form calcite due to the faster kinetics of carbonation compared to polymerization of the CSH-layered structures. Further increasing the temperature to 200°C generated the strong peaks characteristic of pectolite phase. This indicates that at higher temperatures (above 180°C) and with the presence of Na^{+} as an accelerator, the tobermorite-like CSH structures tend to transit to more hydrothermally stable structures like pectolite. The higher stability of pectolite compared to tobermorite structure could be assigned to the microscopic discriminations in their layered crystalline structures.

Tobermorite has a stacked layered structure with an interlayer space separating two adjacent layers. The interlayer space in $11\text{ \AA}$ tobermorite is mostly occupied by water molecules and Ca^{2+} ions. However, pectolite is an anhydrous crystalline calcium silicate with no interlayer spacing containing water. Therefore, at elevated temperatures, $11\text{ \AA}$ tobermorite has a greater tendency to lose the water content in the interlayer space and transform into more stable anhydrous pectolite structure. This is also in agreement with the results reported by Zou et al. (2016) and Liu et al. (2013). Therefore, 180°C was found as an optimum reaction temperature to synthesize pure $11\text{ \AA}$ tobermorite. Henceforth, it was applied to the next set of experiments to investigate the effect of Ca/Si.

6.3.1.4. Effect of Ca/Si

As mentioned earlier, CSH structure is a defect tobermorite structure and the degree of deviation strongly depends on the Ca/Si. To investigate the impact of Ca/Si on the microstructure of the synthetic $11\text{ \AA}$ tobermorite, a range of 0.83~2.0 values was studied. The XRD patterns of the

samples synthesized with the Ca/Si within the aforementioned range at 180°C for 5h using 0.5M of activator concentration are shown in Figure 6-5. The results showed that pure single-phase

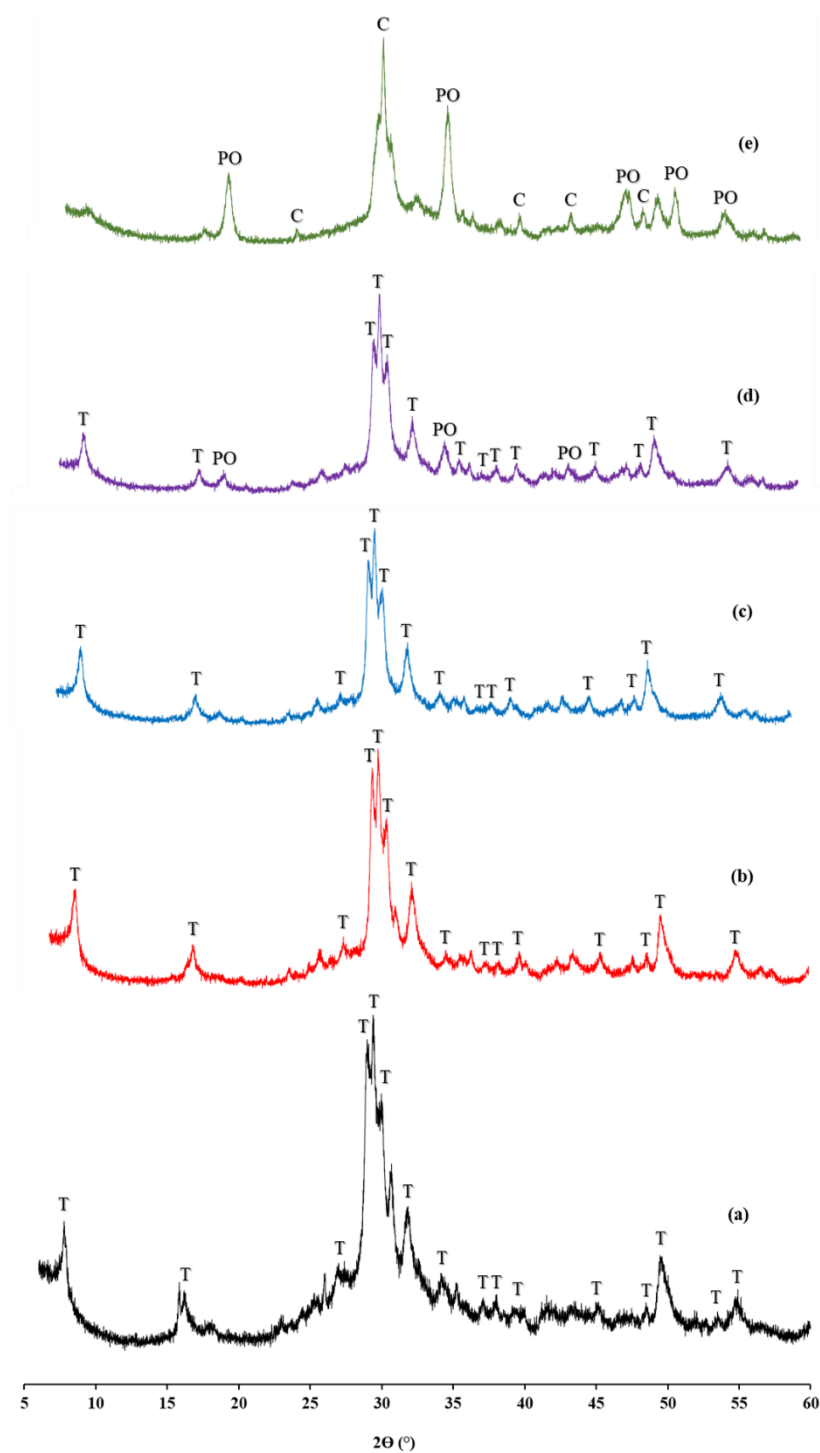


Figure 6-5. XRD patterns of the samples synthesized at 180°C for 5h and 0.5M of activator concentration obtained with Ca/Si of (a) 0.83, (b) 1.0, (c) 1.2, (d) 1.4, and (e) 2.0. Note: T- Tobermorite; PO-Portlandite; C-Calcite.

tobermorite was observed at lower Ca/Si values (i.e. 0.83, 1.0, and 1.2). An increment of Ca/Si to 1.4 emerged the formation of tiny portlandite phase. At the Ca/Si of 2.0, the 11 Å tobermorite characteristic peaks disappeared, while relatively strong reflections of portlandite and calcite phases were detected. This could be attributed to the fact that the CSH structures are highly disordered to be X-ray sensitive at high Ca/Si values (especially Ca/Si over 1.45). Therefore, their structure could have a significant defect from the ideal tobermorite (Lothenbach and Nonat, 2015).

On the other hand, the variation in the composition of CSHs highly relies on the activity of the ionic species in the equilibrium solution. It has been established that in a three-component CSH system, the highest Ca/Si at equilibrium conditions is restricted to 1.45, since the Ca^{2+} ions' activity is fixed by the portlandite's solubility (Lothenbach and Nonat, 2015; Taylor, 1950). At Ca/Si of 2.0, the Ca^{2+} content may be more than the solubility limit of portlandite; hence, the extra Ca^{2+} precipitated in the form of portlandite crystals.

According to Figure 6-5, the intensity of (002) 11 Å tobermorite reflections gradually faded with the increment of Ca/Si. This is mainly due to the simultaneous gradual reduction of structural order and basal spacing with the evolution of Ca/Si. This also concurs with the results obtained by Bonaccorsi et al. (2005). They pointed out that higher Ca/Si could result in elimination of more bridging and branching sites in the silica “Dreierketten” chain thereby depolymerizing the silica chains. In addition, more Ca^{2+} ions are absorbed in the interlayer spacing to neutralize the net negative charge on the CSH surface (Lothenbach and Nonat, 2015; Bonaccorsi et al., 2005). The effect of the change in the basal $d_{(002)}$ -spacing of the synthetic tobermorite specimens with respect to the variation of Ca/Si is illustrated at a greater magnification in Figure 6-6.

The (002) basal spacing peak exhibited a gradual shift towards the higher 2θ angles with an increment in the Ca/Si. The mean basal $d_{(002)}$ -spacing calculated from the XRD data using JADE

software also showed a decreasing trend with an increase in the Ca/Si. The cumulative effects of shortening the silica chain length and absorbance of more Ca^{2+} ions in the interlayer spacing with Ca/Si evolution could be the reason for reduction in the basal $d_{(002)}$ -spacing of the 11 Å tobermorite. As a conclusion, Ca/Si of 0.83 is the optimal starting value to synthesize CSHs with closer structural similarity to the ideal 11 Å tobermorite.

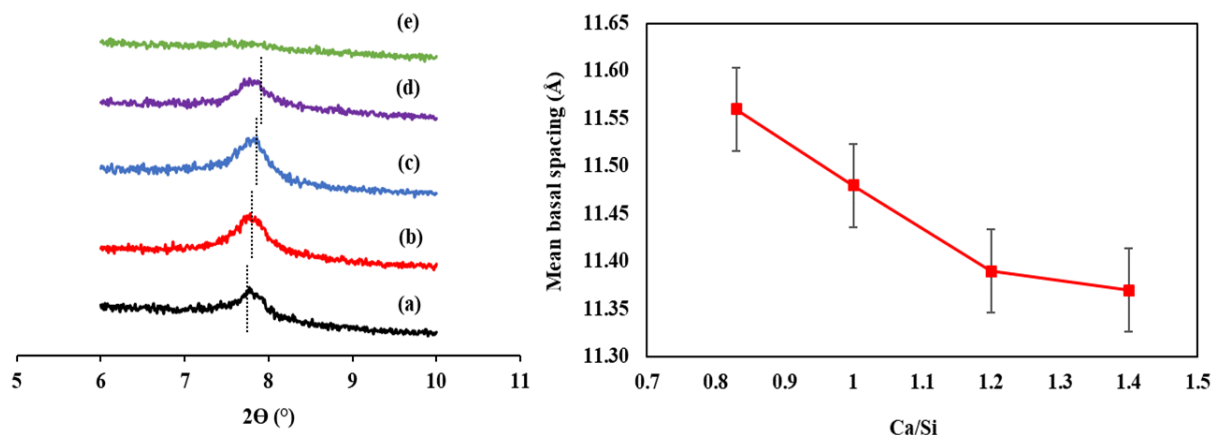


Figure 6-6. Change in the basal $d_{(002)}$ -spacing versus Ca/Si of: (a) 0.83, (b) 1.0, (c) 1.2, (d) 1.4, and (e) 2.0.

6.3.1.5. Effect of Al substitution on the microstructure

According to the XRD patterns, optimal parameters for the synthesis of 11Å tobermorite using WGC are the reaction time of 5h, activator concentration of 0.5M, reaction temperature of 180°, and Ca/Si of 0.83. Going forth, this sample synthesized with the aforementioned conditions would be referred as “WGC-A-T”. The main hypothesis in this study was that this sample could be Al-substituted 11 Å tobermorite due to the partial substitution of the Al released from the WGC precursor with some Si sites in the dreierketten chain. To investigate whether this hypothesis is correct, a reference sample was synthesized under the same values of synthesis parameters using fumed silica. This sample is referenced as a non Al-substituted 11 Å tobermorite and labeled as “Ref.-T” here on.

The XRD patterns of the WGC-A-T and Ref.-T samples are illustrated in Figure 6-7, representing the impact of Al substitution on the structure of the 11 Å tobermorite. The basal d-spacing values of 0.304 nm, 0.275 nm, and 0.168 nm are attributed to the (110), (200), and (020) reflections of the 11 Å tobermorite crystalline planes, respectively (Taylor, 1997; Sun et al., 2006). The data indicated that the dimensions of (200) and (020) basal spacing values exhibited negligible deviation between WGC-A-T and Ref.-T.

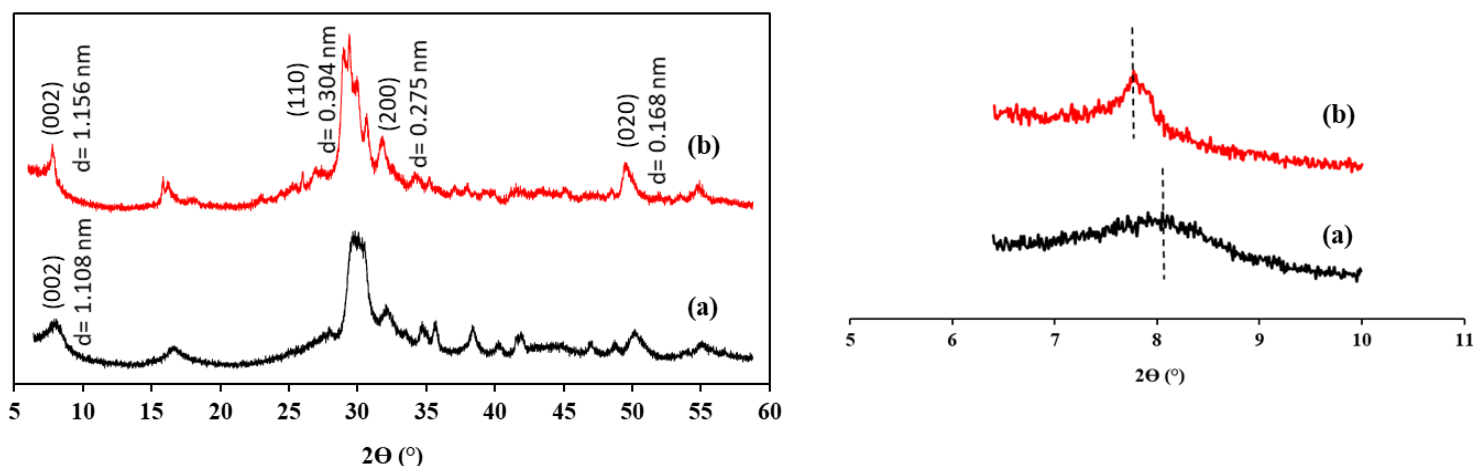


Figure 6-7. Effect of Al substitution on the 11 Å tobermorite microstructure using XRD for (a) Ref.-T, and (b) WGC-A-T samples.

Both WGC-A-T and Ref.-T exhibited a relatively strong (002) peak at around 8° 2 θ . According to Figure 6-7, the (002) reflection corresponding to WGC-A-T shifted slightly to lower 2 θ angles compared to the Ref.-T. This trend is also shown at a greater magnification in Figure 6-7. The basal (002) d-spacing value of Ref.-T was roughly 1.108 nm, which increased to 1.156 nm for WGC-A-T sample. This could be attributed to the substitution of the Al content released from WGC precursor into the WGC-A-T tobermorite microstructure (Sun et al., 2006). The higher intensity of (002) reflection in WGC-A-T may also reflect the Al presence in the interlayer spacing.

6.3.2. EDX analysis

The elemental composition results for WGC-A-T and Ref.-T tobermorite samples obtained via EDX analysis are presented in Table 6-2, and compared to that of the natural tobermorite. The tobermorite samples are primarily composed of Ca and Si elements. EDX analysis confirmed the presence of Al in WGC-A-T tobermorite, while roughly no Al was detected in Ref.-T tobermorite. This could be attributed to the Al incorporation (released from the WGC precursor) within the WGC-A-T tobermorite microstructure. The Ref.-T exhibited a Ca/Si of 5/5.77, while the WGC-A-T tobermorite showed a Ca/Si of 5/5.68. This indicates that Al incorporation decreased the relative Si content and increased the overall Ca/Si.

Table 6-2. The elemental composition of WGC-A-T and Ref.-T tobermorites.

Elements	Ca		Si		Al		Ca/Si	Tobermorite composition using atomic ratios
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)		
WGC-A-T	24.01	12.01	17.71	13.65	1.08	0.87	0.87	Ca ₅ Si _{5.68} Al _{0.36}
Ref.-T	31.38	17.05	22.53	19.7	-	-	0.86	Ca ₅ Si _{5.77}
Natural tobermorite							0.83	Ca ₅ Si ₆

The degree of polymerization of the silica chain in a CSH structure strongly depends on the Ca/Si ratio and amount of Al incorporation, according to the results obtained by Sun et al. (2006). They reported that the polymerization degree of the silica chain reduced as the Ca/Si elevated from 0.8 to 1.7. On the contrary, the degree of polymerization in silica chain tend to increase with the increment in Al substitution. Hence, the CSH microstructure could attain superior polymerization via improved Al incorporation.

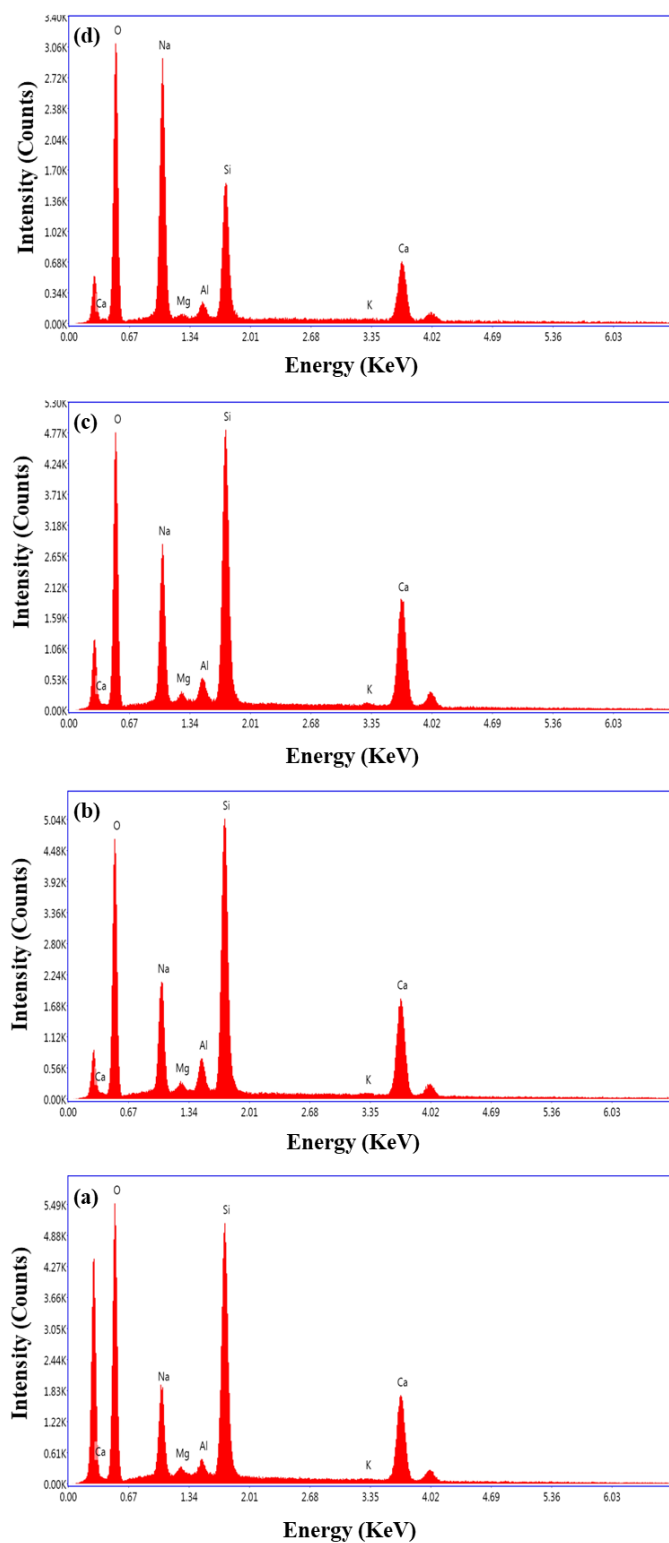


Figure 6-8. EDX elemental analysis of the tobermorite samples synthesized in the second set of experiments at activator concentrations of (a) 0.5M, (b) 1.0M, (c) 2.0M, and (d) 4.0M.

Figure 6-8 illustrates the elemental analysis of the tobermorite samples synthesized via the second set of experiments (Table 6-1) with the activator concentration ranging between 0.5~4.0M. The analysis showed a gradual increment in the Na^+ content of the samples, as the activator concentration increased from 0.5 to 4.0M. This is in agreement with the XRD results (Figure 6-3) indicating the gradual transformation of tobermorite-like CSH structure to a pectolite phase at higher alkali activator (Na^+ content) concentrations.

6.3.3. SEM analysis

The morphologies of the WGC precursor and tobermorite samples synthesized via the first set of experiments (Table 6-1) with the curing time between 2~72h are shown in Figure 6-9. At 2h, a gel-like morphology was observed corresponding to the formation of an amorphous CSH gel on the surface of the agglomerated cullet particles (Figure 6-9b). Due to the short reaction time, this gel could not be crystallized to form tobermorite fibers, which is in agreement with the results obtained by XRD (Figure 6-2). At the reaction time of 5h, high amount of platy-shaped and needle-like tobermorite crystallites were observed, which have also been commonly reported by other studies (Sun et al., 2006; Ding et al., 2017). At 10h, crystallites with broom-like shapes were observed due to the emergence of the pectolite phase. The SEM analysis clearly shows the change in morphology with increment in reaction time as the tobermorite transforms to a more hydrothermally stable pectolite phase. This is also in agreement with the XRD results (Figure 6-2). Further increment in reaction time to 24h and 48h resulted in higher density of broom-like crystals indicating more pectolite formation. As the reaction prolonged to 72h, more pectolite whiskers with longer broom-like crystals were observed. This indicates that prolonged reaction times favor the pectolite phase formation, resulting in the growth of elongated broom-like whiskers.

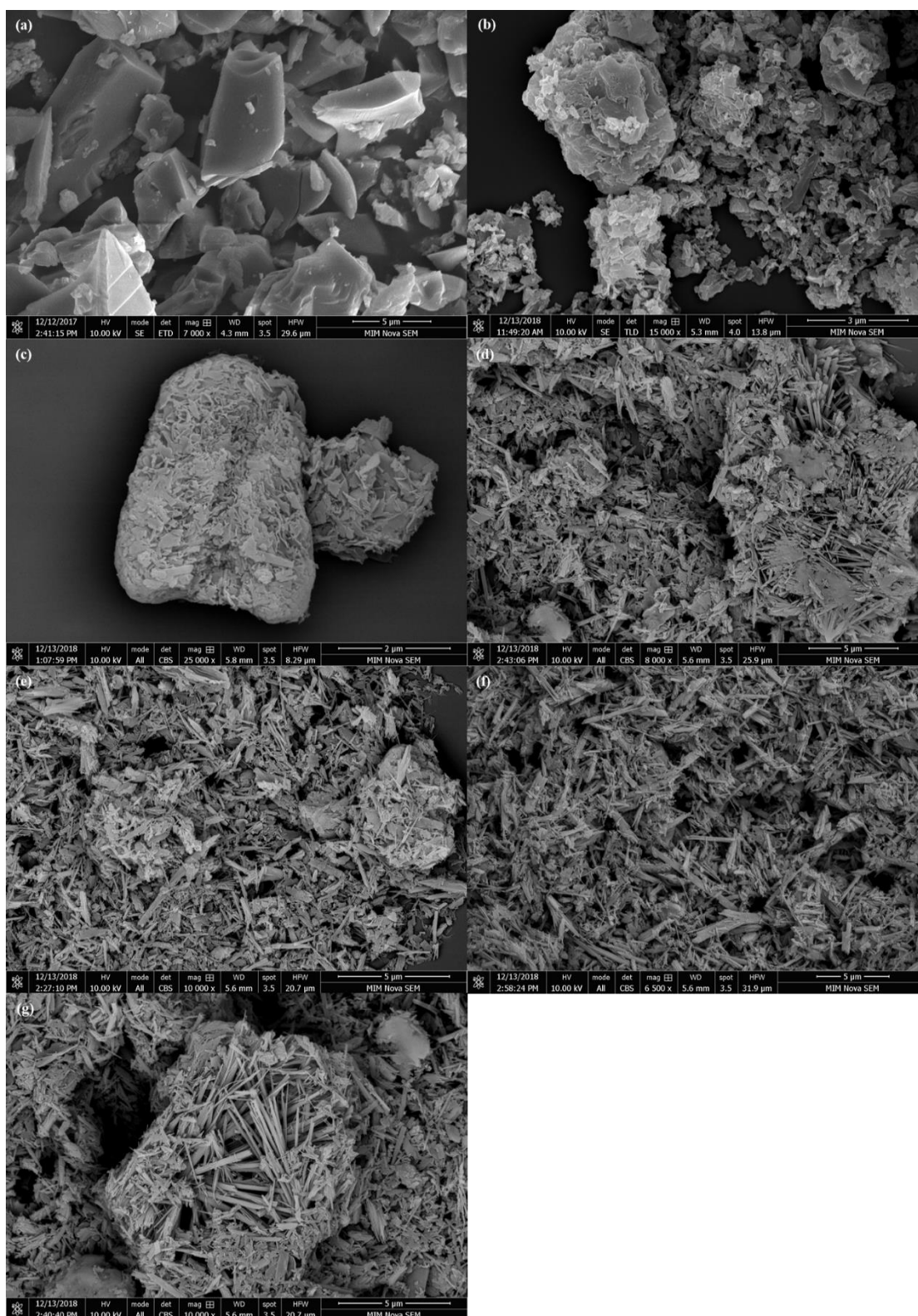


Figure 6-9. SEM of the (a) WGC precursor and tobermorite samples synthesized via the first set of experiments with reaction time of (b) 2h, (c) 5h, (d) 10h, (e) 24h, (f) 48h and (g) 72h.

The morphologies of the WGC-A-T and Ref.-T tobermorite samples are illustrated in Figure 6-10. The WGC-A-T morphology exhibited a remarkable difference compared to the Ref.-T. In the former, massive acicular crystals were detected on the surface of cullet particle, while the latter had more broaden platy-like morphology. This variation in morphology could be due to the effect of Al incorporation on the growth of crystals.

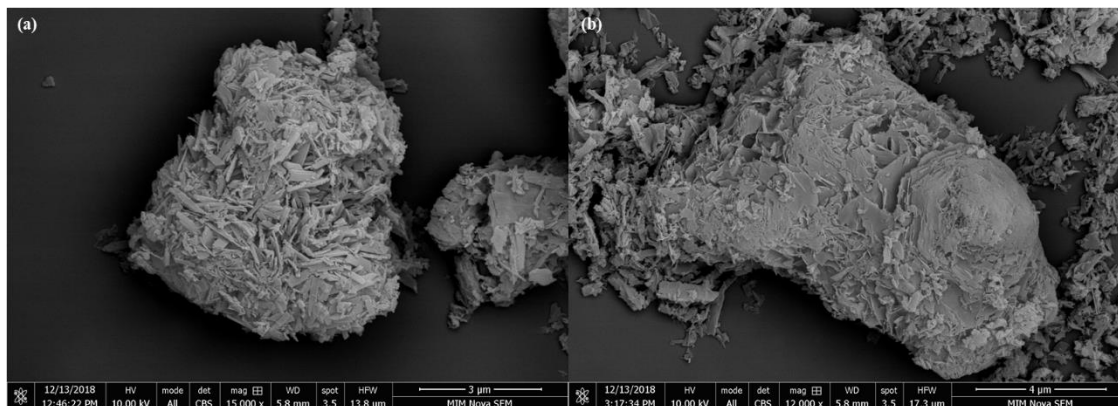


Figure 6-10. SEM of the (a) WGC-A-T and (b) Ref.-T tobermorite samples.

This is also in agreement with the results reported in the literature. For instance, Maeda et al. (2011) reported that the addition of Al_2O_3 led to the formation of larger fiber-like crystals formed compared to the Al-free reference. In another study by Matekonis et al. (2010), needle-like and platy-shaped crystals were observed for the Al-free tobermorite. With the addition of Al_2O_3 , the needle-like crystals disappeared and elongated plates were formed.

6.3.4. FTIR analysis

The FTIR spectrum of the WGC precursor as well as the WGC-A-T and Ref.-T tobermorite samples were illustrated in Figure 6-11. Six bands at 3475 cm^{-1} , 2358 cm^{-1} , 1646 cm^{-1} , 1024 cm^{-1} , 882 cm^{-1} , and 538 cm^{-1} were observed on the spectrum of the WGC precursor. The stretching mode of the Si-OH silanol hydrogen group within the glass matrix as well as the stretching and bending vibrational modes of the O-H molecule are indicated by the band at 3475 cm^{-1} (Naresh and Ham,

2016). The vibrational modes of the non-bridging O-H bonds are also attributed to the band at 2358 cm^{-1} (Naresh and Ham, 2016). The vibration of the bridging Si-O asymmetric stretching generated within the silica tetrahedrals as well as the O-H group vibrational modes are represented by the band at 1646 cm^{-1} (Naresh and Ham, 2016). The vibrational modes of the Si-O-Si bonds within the structural matrix of silica tetrahedrals are also attributed to the several bands emerged between the range of 1100 cm^{-1} - 500 cm^{-1} (Naresh and Ham, 2016).

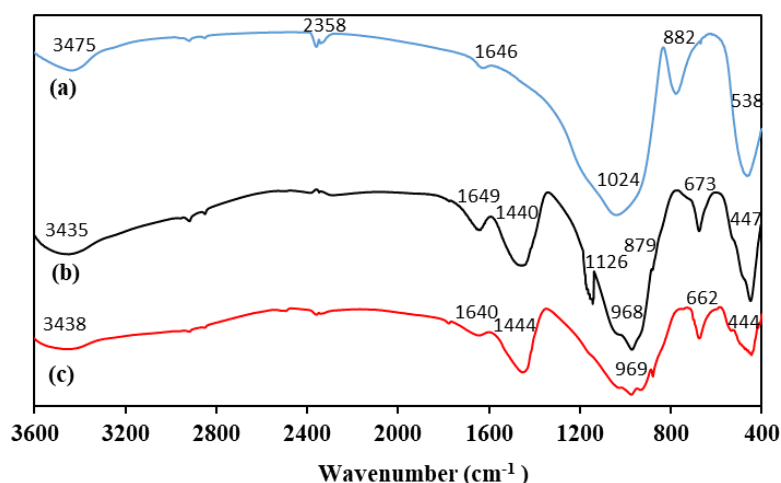


Figure 6-11. FTIR spectrum of the (a) WGC precursor, (b) WGC-A-T, and (c) Ref.-T tobermorite samples.

In the case of WGC-A-T tobermorite shown in Figure 6-11 (b), the bands that emerged at 447 cm^{-1} and 673 cm^{-1} are assigned to the vibrational bending of Si-O-Si and Si-O (Q^1) bonds, respectively. The band observed at 968 cm^{-1} is ascribed to the stretching vibration of Si-O (Q^2). The vibrational band corresponding to the Si-O (Q^3) aroused at 1126 cm^{-1} (García-Lodeiro et al., 2008). The Ref.-T tobermorite spectrum also resembled the spectra of the WGC-A-T. The vibrational band of Si-O (Q^2) stretching in WGC-A-T tobermorite showed greater absorption intensity compared to the Ref.-T, probably due to the incorporation of Al in the silica chains (Guo et al., 2017). The wavenumber of the band showed negligible differences in both samples, representing that Al

incorporation did not have a great impact on shifting the vibrational frequency of the Si-O (Q²) stretching.

Carbonation of the samples occurred due to the presence of vibrational bands at around 1440 cm⁻¹. The vibrational bending of the Si-O-Si bond showed similar adsorption capacity for both samples. However, the band position in Ref.-T shifted slightly from 662 cm⁻¹ to the higher value of 673 cm⁻¹ in WGC-A-T indicating the increase in degree of polymerization in the silica dreierketten chains with the incorporation of Al. The band ascribed to the bending vibration of Q³ also aroused at 879 cm⁻¹ (Lippmaa et al., 1980). The vibrational band assigned to the bending of Si-O (Q¹) was observed at 447 cm⁻¹ in WGC-A-T and at a similar value of 444 cm⁻¹ in Ref.-T. Both WGC-A-T and Ref.-T samples exhibited similar vibrational bands ascribed to the stretching of O-H bond as well as H₂O molecules. The vibrational band of H-O-H appeared at 1649 cm⁻¹. The vibrational stretching of the H-O-H emerged at 3435 cm⁻¹ and 3438 cm⁻¹ for WGC-A-T and Ref.-T tobermorites, respectively.

6.3.5. Differential Scanning Calorimetry (DSC) analysis

Figure 6-12 illustrates the DSC curves of the Ref.-T as well as WGC-A-T tobermorites. Three endothermic peaks were observed in the DSC spectrum of Ref.-T tobermorite at 55 °C, 131 °C, and 820 °C. However, a relatively sharp exothermic peak also emerged at 680 °C. At the initial stages, tobermorite exhibited a stable and ordered crystalline microstructure. The first endothermic peak at 55 °C was ascribed to the loss of free water, while the second peak at 131 °C corresponds to the loss of interlayer water molecules. This dehydration is followed by a reduction in the interlayer spacing and the shrinkage of the 11 Å tobermorite to the 9 Å tobermorite. The exothermic peak at 680 °C is attributed to the dehydroxylation and cleavage of the Si-O-H bonds. This indicates the probable destruction of the tobermorite microstructure and its transformation to

a more metastable, amorphous, and disordered microstructure. According to Maeshima et al. (2003), synthetic or natural 11 Å tobermorite tend to transform to an anhydrous form of wollastonite (CaSiO_3) at the elevated temperatures close to 850 °C. A sharp endothermic peak at 820 °C was observed for Ref.-T tobermorite, which can be inferred as recrystallization to a wollastonite-like structure.

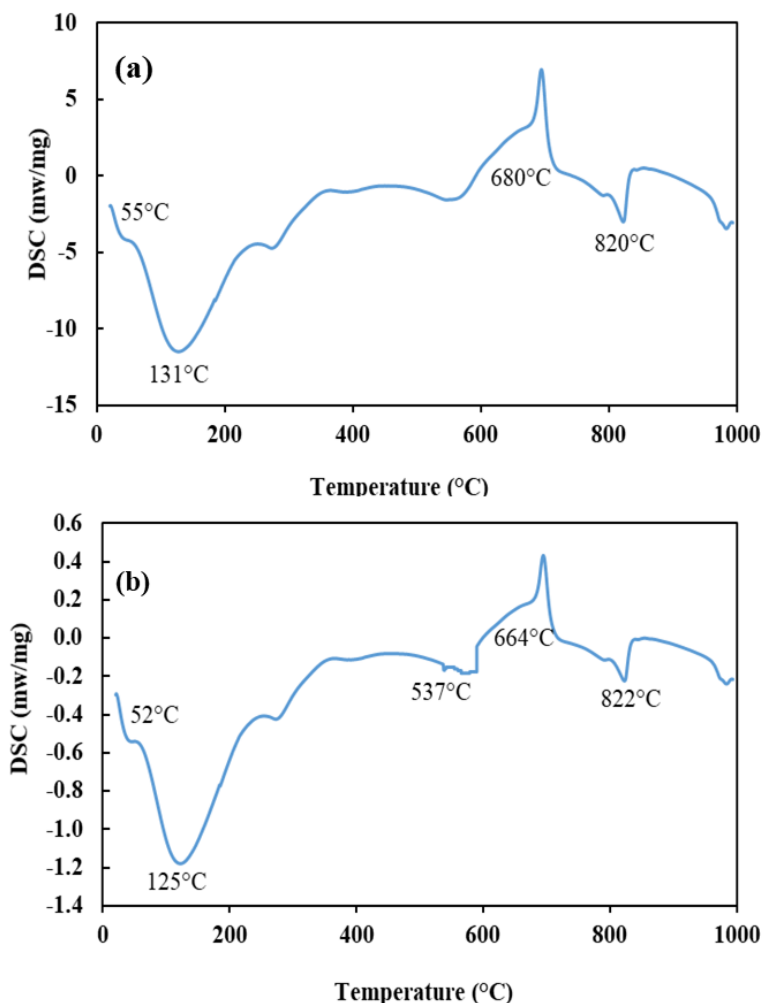


Figure 6-12. DSC spectrums of (a) Ref.-T and (b) WGC-A-T tobermorite samples.

In the case of WGC-A-T tobermorite, the DSC spectrum showed roughly similar locations for the exothermic and endothermic peaks. The main difference was the presence of a weak endothermic peak at 537 °C ascribed to the Al-O bond cleavage. The presence of this peak denotes Al

substitution within the microstructure of WGC-A-T tobermorite. This is also in agreement with the XRD results (section 6.3.1.5.).

6.3.6. Nuclear Magnetic Resonance (NMR) analysis

6.3.6.1. ^{29}Si MAS-NMR analysis

^{29}Si MAS-NMR analysis represents structural information regarding the local environment of silicate units in the silica-based solids. Tetrahedrals of silica are often indicated by Q units and $\text{Q}^n(\text{mAl})$ represents a silica unite connected to n adjacent tetrahedrals, out of which m are tetrahedrals of alumina. In this notation, 0 to 4 is the common range for m and n. A single silica connected to another silica unite, end-chain silica tetrahedrals, and isolated pairing tetrahedrals are all merged as a Q^1 structure. A silica unite connected to two other silica tetrahedrals is represented either as a Q^2_{P} structure if located at a pairing site or Q^2_{B} if located at a bridging site. A pairing silica tetrahedra connected to one silica site and one alumina tetrahedron located at a bridging site is often represented as $\text{Q}^2_{\text{P}}(1\text{Al})$ (García-Lodeiro et al., 2008). A bridging silica unite crosslinking two adjacent silica layers by branching with a bridging silica tetrahedron from the adjacent layer is indicated as Q^3_{B} . If the bridging site from the adjacent layer is an alumina tetrahedron, the mentioned silica unit is represented as $\text{Q}^3_{\text{B}}(1\text{Al})$. Table 6-3 shows the commonly reported ranges of chemical shifts for the Q^n structural tetrahedron in most silica-based solids (Sun et al., 2006; García-Lodeiro et al., 2008; Lippmaa et al., 1980).

The layered microstructure of tobermorite consists of central CaO sheets where the Ca^{2+} ions are heptahedrally coordinated with oxygen atoms. The CaO sheets share their oxygen atoms with the pairing tetrahedrals of the silica chains arranged in a dreierketten structure on the top and bottom of the main CaO layer (Lothenbach and Nonat, 2015). Single crystal X-ray technique was used by Merlino et al. (1999) to investigate the natural tobermorite crystal structure. They reported that the

heptahedrally coordinated CaO sheets that extend along the b-axis and parallel to the silica dreierketten chains play a key role in the formation of the layered structure. In the case of anomalous 11 Å tobermorite, crosslinking of the double silica chains may occur via the branching of the two adjacent bridging sites. The interlayer space between layers is mostly occupied by free Ca^{2+} and water molecules.

Table 6-3. Ranges of chemical shifts for the Q^n structural tetrahedron in most silica-based solids (Sun et al., 2006; García-Lodeiro et al., 2008).

Si-O-T connection type	Chemical shift (ppm)	Q^n structural tetrahedron
Isolated dimers/ end-chain silicate units	-78 to -84	Q^1
	-76 to -81	Q^1 (1Al)
Silicate units in the middle chain	-81 to -89	$\text{Q}^2_{\text{B}}/ \text{Q}^2_{\text{P}}$
	-80 to -85	Q^2_{P} (1Al)
Silicate units in the branching sites of the chain and layers	-86 to -94	Q^3
	-90 to -95	Q^3_{B} (1Al)
Silicate units connect networks of three-dimensional structures	-96 to -126	Q^4

The ^{29}Si MAS-NMR quantitative and qualitative spectrum analysis could shed light on the extent of polymerization degree in a tobermorite-like CSH microstructure. The change in the intensity of the Q^n peaks is the main representative of the qualitative analysis. In other words, the dreierketten chain has a superior degree of polymerization if the intensity of Q^2 peak is higher. The ^{29}Si MAS-NMR spectra of the Ref.-T and WGC-A-T tobermorite samples are illustrated in Figure 6-13. The Ref.-T tobermorite spectrum exhibited four peaks located at -79.8 ppm, -81.9 ppm, -83.8 ppm, and -93.5 ppm chemical shifts, respectively. The peaks at -79.8 ppm and -81.2 ppm are attributed to the Q^1 and Q^2_{B} , respectively. The peaks at -83.8 ppm and -93.5 ppm represent Q^2_{P} and Q^3_{B} ,

respectively. Figure 6-13 (b) illustrates the ^{29}Si MAS-NMR spectrum of the WGC-A-T tobermorite sample. Six peaks at -78.0 ppm, -80.7 ppm, -81.1 ppm, -82.4 ppm, -90.48 ppm, and -92.4 ppm chemical shifts were observed on the WGC-A-T tobermorite spectrum (Komarneni et al., 1985). The peaks at -78.0 ppm and -81.1 ppm are assigned to the Q^1 and Q^2_{B} , respectively.

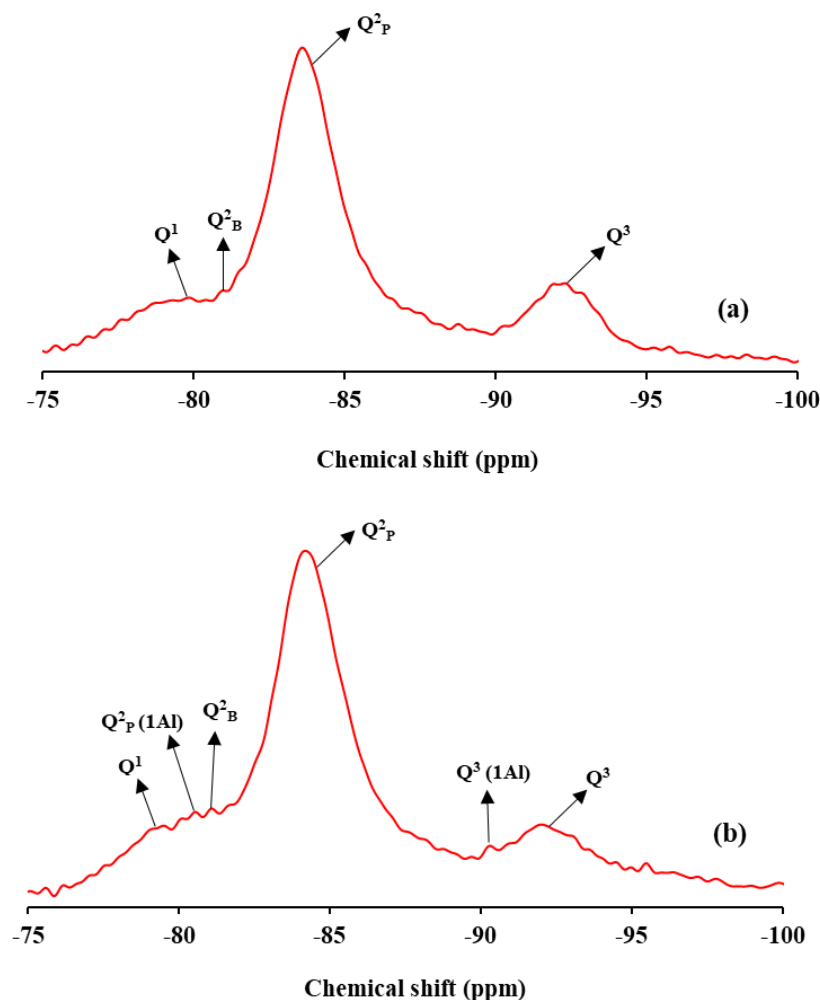


Figure 6-13. ^{29}Si MAS-NMR spectrums of (a) Ref.-T and (b) WGC-A-T tobermorite samples.

The weak shoulder at -80.7 ppm is ascribed to the $\text{Q}^2_{\text{P}}(1\text{Al})$, while the peak at -82.4 ppm represents the Q^2_{P} . The peaks at -90.48 ppm, and -92.4 ppm correspond to the $\text{Q}^3_{\text{B}}(1\text{Al})$ and Q^3_{B} , respectively. The appearance of new peaks, i.e. $\text{Q}^2_{\text{P}}(1\text{Al})$ and $\text{Q}^3_{\text{B}}(1\text{Al})$, on the spectrum of WGC-A-T tobermorite signifies the substitution of Al from the WGC precursor into the layered

microstructure. In this case, Al could be substituted at the bridging and branching sites within the dreierketten silica chains of the WGC-A-T tobermorite.

6.3.6.2. ^{27}Al MAS-NMR analysis

Different coordination environments of Al and its interaction with the CSH microstructure are determined using ^{27}Al MAS-NMR data. Generally, Al is available in cement hydration products with three structural coordinations of IV, V, and VI (Sun et al., 2006). The resonance peaks of Al_{IV} , Al_{V} , and Al_{VI} are expected to appear at 50~70 ppm, 30~40 ppm, and 0 ppm ranges of chemical shifts, respectively (Sun et al., 2006; Komarneni et al., 1985). The Al atoms that coordinate in tetrahedrals are assigned as Al_{IV} (tetrahedrally coordinated) and they play a key role in forming networks within the microstructure of CSH. The Al atoms that coordinate with six other oxygen atoms are known as Al_{VI} (octahedrally coordinated) and they mostly modify the structural network of CSH. The remaining Al atoms interacting with the CSH structure are denoted as Al_{V} (pentahedrally coordinated).

The tetrahedrally coordinated Al_{IV} atoms have a great tendency to be substituted into the middle chain Q^2_{B} bridging and Q^3_{B} branching positions. In one study, Anderson (2003) observed a resonance peak at lower chemical shifts for a hydrated cement paste sample and reported that this peak may not be attributed to the Al_{IV} substituted into the CSH structure. They believed that it is more likely ascribed to a new amorphous phase of aluminate hydrate such as $\text{Al}(\text{OH})_6^{3-}$, through which Al is octahedrally coordinated (Al_{VI}). In the case of pentahedrally coordinated Al_{V} , the substitution preferentially may occur for the charge balancing Ca^{2+} ions occupying the interlayer spacing. The type of coordination environment of Al atoms in the hydrated cement paste is strongly influenced by the Ca/Si of the paste (Lothenbach and Nonat, 2015; Anderson, 2003).

The ^{27}Al MAS-NMR spectrum of the WGC-A-T tobermorite sample is illustrated in Figure 6-14. Two peaks at 59.22 ppm and 66.12 ppm chemical shifts are both attributed to the resonance of the Al_{IV} coordination. These peaks are in agreement with the results reported in recent studies for the 11 Å tobermorite (Guo et al., 2017; Wang et al., 2017). The peaks corresponding to the resonance of the Al_{V} and Al_{VI} were not observed on the spectrum of the WGC-A-T tobermorite sample, indicating the predominance of the Al_{IV} coordination environment.

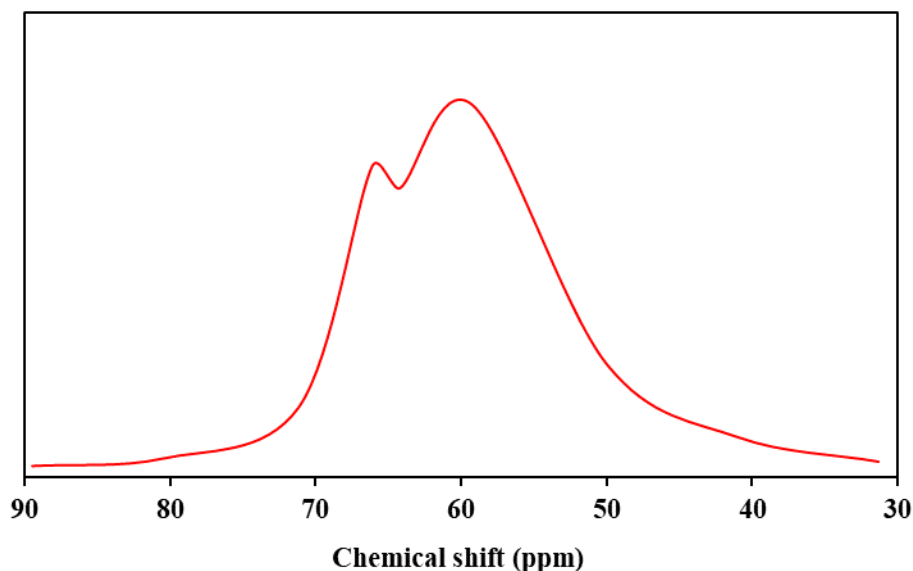


Figure 6-14. ^{27}Al MAS-NMR spectrum of the WGC-A-T tobermorite sample.

The emergence of two distinct peaks for the Al_{IV} coordination could be ascribed to two different lattice environments where Al is substituted for Si. The peak at 66.12 ppm corresponds to the substitution of Al_{IV} for the Q^2_{B} bridging middle chain sites, while the resonance at 59.22 ppm is related to the Al_{IV} substitution for the Q^3_{B} branching tetrahedrals (Anderson, 2003). The structures of the two mentioned distinct Al_{IV} positions were resolved by Houston et al. (2009) by means of the ^{27}Al MAS-NMR analysis. They also reported that Al preferentially occupied the Q^2_{B} bridging and Q^3_{B} branching positions. This suggests that Al plays a key role in linking the chains of

polymeric silica in the course of crystal growth, resulting in the creation of silica tetrahedrals joined by the Al bridging and branching sites. The results also satisfy the XRD inference explained in section 6.3.1.5.

6.4. Conclusions

This study investigated the microstructure of the Al-substituted 11 Å tobermorite synthesized using the WGC as the precursor. The suitable values for the key synthesis parameters were 180 °C reaction temperature, 5h of reaction time, 0.5M of alkali activator concentration, and Ca/Si of 0.83. The influence of Al substitution was examined using various techniques including XRD, EDX, SEM, FTIR, TGA/DSC, and ^{29}Si MAS-NMR and ^{27}Al MAS-NMR analysis. The XRD results clarified that Al ions could be substituted within the tobermorite microstructure and subsequently increase the interlayer spacing. The EDX results demonstrated that Al substitution reduced the relative Si content and increased the overall Ca/Si ratio. The Al incorporation remarkably changed the tobermorite morphology from platy-like shape to acicular crystallites, based on SEM results. TGA/DSC analysis exhibited a new weak endothermic shoulder ascribed to the Al-O bonds cleavage on the spectrum of the tobermorite synthesized using WGC. The cumulative results for FTIR, ^{29}Si MAS-NMR and ^{27}Al MAS-NMR analysis also confirmed that the polymerization state of the dreierketten silica chains improved with the Al substitution. The results obtained in this study provide a better understanding of the application of the Al-based wastes as cementitious materials in construction and as adsorbents in the environmental remediation sector, in terms of both atomic- and micro-scale. Further investigation regarding the effect of Al-substituted CSH on the mechanical properties of the hydrated cement paste and mortars needs to be conducted to better clarify the role of Al-substituted binder in concrete micro-scale behavior.

Chapter 7. Engineering significance

Canada recycles less than one-half of the estimated 850,000 tons container glass in the market place on an annual basis. It is important to create a market-place for value-added utilization of recycled glass to drive recycling rates and reduce disposal in landfills. Applications in utilizing recycled crushed glass as an aggregate material in concrete and asphalt, reflective beads for road paints, and road bed aggregates have been reported. However, high recycling rate of the glass cullet towards manufacturing of post-consumer glass requires relatively sophisticated post-processing steps to prepare a clean material, which makes these processes economically cost-prohibitive. Current glass separation and screening activities that are employed in material diversion facilities across Canada leave a glass stream that can include contaminants including mixed-colored cullet, ceramics, trace metals, hard plastics (i.e. bottle caps), and other organics (i.e. some paper, etc).

The proposed research could provide a new market for this relatively impure recycled glass aggregate, if crushed and pulverized glass can be utilized as a feedstock for zeolites and tobermorite synthesis. Converting waste glass cullet to zeolites and tobermorite not only solves the challenge of large waste glass landfilling, but also produces value-added products with a wide variety of applications within chemical, petrochemical, environmental, and construction sectors. Compared to the traditional synthesis procedures using costly chemical-grade reagents, production of zeolites and tobermorite utilizing a cheap and readily-available precursor such as waste glass could remarkably reduce the synthesis costs. Application of microwave radiation as a novel source of energy in the present work was approved to reduce the synthesis time considerably from couple of days in conventional heating to virtually couple of minutes. This will make the microwave radiation a green and energy-efficient technology that could be a promising alternative heat source

for a feasible commercial zeolitization. The results obtained in this study would shed light on optimizing the microwave radiation in a way that highly crystalline phases with lower energy consumption could be crystallized.

This work also offered an environmentally friendly option to reduce the amount of water usage for the zeolitization process by utilizing landfill leachate as a novel alternative aqueous phase. This idea could save a huge amount of fresh water (roughly 20 metric tones per each metric tones of the synthesized zeolite). Hence, wastewater generation could be minimized by reusing landfill leachate as the solvent that could result in a significant reduction of environmental issues and cost of the zeolite synthesis process at large scale. The presence of numerous toxic components including suspended solids, soluble and particulate organics/inorganics, and heavy metals have made the landfill treatment quite complicated and costly. The novel idea developed in this thesis would pave the way for the reusage of two waste streams (i.e. waste glass and landfill leachate) towards the synthesis of value added zeolites. The landfill leachate also could provide the reaction mixture with noticeable alkalinity, alkali and alkali-earth cations, which reduces the concentration of the structure directing agent needed. This could also contribute to the cost reduction of the zeolitization process.

Chapter 8. General conclusions and future recommendations

8.1. Conclusions

The main target of this thesis was to synthesize value-added products including zeolites and 11Å tobermorite out of waste glass cullet (WGC) as a starting precursor using novel energy sources such as microwave (MW) radiation technique. Various analytical techniques were utilized to characterize the specimens including FTIR, NMR, XRD, SEM, TGA, DSC, and EDX. The main overall conclusions obtained in this work are as follows:

1) Several zeolites were synthesized from the beverage WGC using a single-mode MW reactor under autogenous pressure. Two modes of MW radiation were employed i.e constant temperature (MWCT) and constant power (MWCP) without aging the gels. The results obtained by MW synthesis experiments were also compared to those synthesized by conventional heating (CH) method. Highly crystalline zeolites were synthesized by means of MW radiation without aging the specimens indicating the non-essentiality of aging for the synthesis of zeolites with high crystallinity. The results demonstrated the high efficiency of the MW radiation to convert WGC to zeolites rapidly. However, specific radiation conditions should be applied for the synthesis of a zeolite with desirable crystallinity and physiochemical properties. Results revealed that MWCT could be an efficient radiation mode, which rapidly synthesized zeolites under superheating conditions with almost similar properties with the zeolite synthesized by CH. The prolonged synthesis times of several hours in the CH was remarkably declined to few minutes (shortest time was 10 min) in MWCT. However, MWCP was found as an inefficient mode with high energy demand which synthesized poorly crystalline products. It was suggested that the MW apparatus for the promising MWCP radiation should be modified from the closed-mode to an open-mode to

minimize the adverse effects of high vapor pressure generation within a high temperature environment on the nucleation and crystallinity of the products.

2) Similar single-mode MW apparatus was used for the rapid conversion of WGC to zeolites by monitoring the temperature and power through MWCT and MWCP modes. This conversion was accomplished by the application of two synthesis methods; one with a fusion pretreatment (IFS) and the other was solely direct hydrothermal treatment (DHS). Zeolites prepared by IFS were found superior to those synthesized by DHS in terms of crystallinity, indicating much better performance of IFS method. Eliminating the prohibitive effect of Al species on the solubility of the silicates within the WG matrix was found as the probable cause of IFS higher efficiency. The water holding and ion exchange capacities of the IFS zeolite was found to be also greater compared to the DHS one. Extreme vapor pressure and temperature overshoot were also found to have adverse effects on the zeolite nuclei and crystal growth rate. This high pressure/temperature environment could be caused by the intensive interaction of the MW with highly ionic-conductive gels. Our results approved that application of cooling air jet during radiation could properly monitor this overshoot by minimizing the adverse effects of pretty much hot spot zones.

3) The performance of leachates from landfill as an alternative solvent to convert WGC to zeolites in terms of phase types, relative quantities, and crystallinity was evaluated. A detailed comparison between the zeolites synthesized by leachate and DI water as a reference was made. MW reactor was used to convert WGC by monitoring the radiation temperature and power through MWCT and MWCP modes. The results showed that zeolites synthesized by unfiltered leachate had better crystallinity than that of zeolites synthesized using DI water. The availability of cations other than Na^+ in the unfiltered leachate contributed to the ionic conductivity of the gel, hence; more hot spot zone formation occurred that improved the homogenous nucleation and crystallization rate. The

absence of zeolite Na-P1 in the fine filtered leachate gel was also due to the solid filtration and reduced Na^+ concentration compared to the unfiltered leachate. DI water also resulted in a lower fraction of zeolite Na-P1 compared to the unfiltered leachate due to the lower concentration of Na^+ . Zeolites synthesized using the unfiltered leachate provided the least Si/Al ratio indicating better ion exchange and water holding capacities compared to the fine filtered leachate and DI water derived zeolites as confirmed by EDX, TGA and CEC.

4) Conversion of WGC to another value-added product i.e 11Å tobermorite by means of CH was also studied in this work. Well crystalline pure 11Å tobermorite was synthesized under key reaction conditions which were found as follows: 5h of reaction time, temperature of 180°C, activator concentration of 0.5M, and Ca/Si ratio of 0.83. Various analytical techniques including XRD, EDX, DSC, SEM and NMR characterized the mentioned specimen and confirmed the Al substitution within the layered tobermorite microstructure. SEM images confirmed the acicular morphology of Al incorporated tobermorite, while the reference without Al substitution mostly showed a platy-like morphology. The Al incorporation in the structure was also confirmed by DSC due to the presence of a tiny endothermic peak on the spectrum of the WG synthesized tobermorite corresponding to the cleavage of the Al-O bonds. The preferential substitution of the Al within bridging and branching sites and increasing the polymerization degree of the silica dreierketten chains have also been confirmed by the results obtained by NMR and FTIR techniques.

8.2. Future recommendations

8.2.1. Open-mode MW reactor

The results obtained by the second and third chapters indicated that high temperature/pressure environment within the sealed vessel could inhibit large nucleation and deteriorate the crystallinity of the zeolite. It is recommended that the MW reactor configuration is modified with a reflux

condenser to investigate the atmospheric pressure synthesis. The results should then be compared with the results obtained at autogenous pressure in this study. It is likely that atmospheric pressure could favor the nucleation of metastable phases and improve the crystallinity of these phases.

8.2.2. Synthesis using single-mode MW radiation

Most studies conducted experiments to synthesize zeolites from aluminosilicate wastes such as coal fly ash used high radiation powers (up to 1000W) due to the lower density of electromagnetic field in the cavity within a multi-mode MW oven. However, results obtained in this study confirmed that zeolites could be synthesized from WGC at much lower powers (50 to 100W). Hence, application of a single-mode MW reactor instead of a multi-mode reactor for the commercial zeolite manufacturing from WGC is highly recommended.

8.2.3. Large scale MW zeolitization

So far, huge efforts have been made in the literature including the experimental work in the current thesis with a main focus on the lab-scale synthesis of zeolites using MW radiation. However, profound research needs to be conducted on pilot and commercial-scale in order to convert the plentiful sources of WGC globally using industrial MW reactors. Remarkable challenges are still available that may hinder the large-scale application of MW radiation as an alternative energy source for the CH.

8.2.4. Ultrasound synthesis

This work mainly focused on the mechanism of MW interaction with the gel components as well as the effects of MW radiation on the volumetric heating of the reaction mixture, improving the homogenous nucleation, and shortening the crystallization time due to the rapid temperature rise-up. However, other novel energy sources such as ultrasound could also have promising impacts on the reaction kinetics such as fast nucleation and crystal growth. Therefore, synthesis of zeolites

from WGC using novel ultrasound radiation could also be an interesting topic, which is recommended for the future studies.

8.2.5. Optimal synthesis conditions of the 11Å tobermorite

Even though most studies including this work focused on synthesizing pure well crystalline 11Å tobermorite, the precise conditions at which it has the most hydrothermal stability are still unknown. Hence, further investigation on finding optimal synthesis conditions including precursor type, reaction time, temperature, activator type, concentration, and Ca/Si ratio and their effects on the stability, purity, and crystallinity of tobermorite is highly recommended. The mentioned required investigations will also shed light on the complicated transformation mechanism to more thermodynamically stable phases such as xonotlite and pectolite.

8.2.6. Assessment of the 11Å tobermorite properties

Majority of the recent investigations including this work tried to mainly study the microstructure, key synthesis parameters, and interaction of Al with the layered tobermorite microstructure. However, to the best of our knowledge, there is lack of information in the literature regarding the assessment of the synthesized tobermorite properties. Hence, evaluating the physical, chemical, and mechanical properties of the prepared Al substituted 11Å tobermorite including compressive strength, tensile strength, fire resistance capacity, and ion exchange capacity is also recommended. Thorough assessment of these properties will enable us to manipulate the microstructure to gain the best properties for a specific application particularly in construction and environmental sectors.

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