GLASS POWDER BLENDED CEMENT HYDRATION MODELLING

Modélisation de L’hydratation du Ciment Composé avec Poudre de Verre

Thèse de doctorate ès sciences appliquées
Spécialité : génie civil

List of Jury

James J. Beaudoin, LLD, Ph.D., F.R.S.C., P.Eng
Arezki Tagnit-Hamou, Ph.D., Eng.
Kenneth W. Neale, Ph.D., Eng.
Pierre-Claver Nkinamubanzi, Ph.D.

Huda SAEED

Sherbrooke (Québec), CANADA

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To my FAMILY

Usama & Nour
Abstract

The use of waste materials in construction is among the most attractive options to consume these materials without affecting the environment. Glass is among these types of potential waste materials. In this research, waste glass in powder form, i.e. glass powder (GP) is examined for potential use in enhancing the characteristics of concrete on the basis that it is a pozzolanic material. The experimental and the theoretical components of the work are carried out primarily to prove that glass powder belongs to the "family" of the pozzolanic materials. The chemical and physical properties of the hydrated activated glass powder and the hydrated glass powder cement on the microstructure level have been studied experimentally and theoretically.

The work presented in this thesis consists of two main phases. The first phase contains experimental investigations of the reaction of glass powder with calcium hydroxide (CH) and water. In addition, it includes experiments that are aimed at determining the consumption of water and CH with time. The reactivity, degree of hydration, and nature of the pore solution of the glass powder-blended cement pastes and the effect of adding different ratios of glass powder on cement hydration is also investigated. The experiments proved that glass powder has a pozzolanic effect on cement hydration; hence it enhances the chemical and physical properties of cement paste. Based on the experimental test results, it is recommended to use a glass powder-to-cement ratio (GP/C) of 10% as an optimum ratio to achieve the best hydration and best properties of the paste. Two different chemical formulas for the produced GP C-S-H gel due to the pure GP and GP-CH pozzolanic reaction hydration are proposed. For the pure GP hydration, the produced GP C-S-H gel has a calcium-to-silica ratio (C/S) of 0.164, water-to-silica ratio (H/S) of 1.3 and sodium/silica ratio (N/S) of 0.18. However, for the GP-CH hydration, the produced GP C-S-H gel has a C/S ratio of 1.17, H/S ratio of 2.5 and N/S ratio of 0.18.
In the second phase of this research, theoretical models are built using a modified version of an existing cement hydration modelling code, “CEMHYD3D”, to simulate the chemical reaction of the activated glass powder hydration and glass powder in cement. The modified model, which is referred to as the “MOD-model” is further used to predict the types, compositions and quantities of reaction products. Furthermore, the glass powder hydration data, which is obtained experimentally, is incorporated into the MOD-model to determine the effect of adding glass powder to the paste on the process of cement hydration and resulting paste properties. Comparisons between theoretical and experimental results are made to evaluate the developed models. The MOD-model predictions have been validated using the experimental results, and were further used to investigate various properties of the hydrated glass powder cement paste. These properties include, for example, CH content of the paste, porosity, hydration degree of the glass powder and conventional C-S-H and GP C-S-H contents. The results show that the MOD-model is capable of accurately simulating the hydration process of glass powder-blended cement paste and can be used to predict various properties of the hydrating paste.
Résumé

L'utilisation des déchets dans la construction est l'une des options les plus intéressantes pour la consommation de ces matériaux sans affecter l'environnement. Le verre est l'un de ces types de déchets potentiels. Dans ce travail de recherche, les déchets de verre en poudre, c'est-à-dire la poudre de verre (PV), est examinée pour une utilisation potentielle pour améliorer les caractéristiques du béton sur la base du fait qu'il est un matériau pouzzolanique. Les données expérimentales et théoriques de la recherche ont été réalisées principalement pour démontrer que la poudre de verre appartient à la famille des matériaux pouzzolaniques. Les propriétés chimiques et physiques du ciment contenant de la poudre de verre hydratée activée et de la poudre de verre hydratée au niveau de la microstructure ont été étudiées expérimentalement et théoriquement.

Le travail présenté dans cette thèse est composé de deux phases principales. La première phase de cette recherche contient une investigatrice expérimentale sur la réaction de la poudre de verre avec l'hydroxyde de calcium (CH) et de l'eau. En outre, elle comprend des expériences, qui visent à déterminer la consommation de l'eau et de CH avec le temps. La réactivité, le degré d'hydratation, et la nature de la porosité de la pâte de ciment mélangée avec de la poudre de verre et l'effet de l'ajout de différents rapports de poudre de verre sur l'hydratation du ciment sont également étudiés. Les expériences prouvent que la poudre de verre a un effet pouzzolanique sur l'hydratation du ciment, et donc elle améliore les propriétés chimiques et physiques de la pâte de ciment. Sur la base des résultats d'essai, il est recommandé d'utiliser un rapport optimal poudre de verre-ciment (PV/C) de 10%, pour obtenir une meilleure hydratation et de meilleures propriétés de la pâte. Deux formules chimiques différentes pour les gels de PV CSH produits par la PV seule et par PV-CH réaction pouzzolanique d'hydratation sont proposées. Pour l'hydratation de PV seule, le produit PV-CSH est un gel de calcium-silice ayant un rapport (C/S) de 0,164, un rapport eau- silice (H/S) de 1,3 et un rapport sodium/silice (N/S) de 0,18. Toutefois, pour
l'hydratation PV-CH, le gel de PV CSH produit a un rapport C/S de 1,17, un rapport H/S de 2,5 et un rapport N/S de 0,18.

Dans la deuxième phase de ce travail de recherche, des modèles théoriques sont conçus en modifiant un modèle d'hydratation de ciment pré-existant, "CEMHYD3D" pour simuler la réaction chimique d'hydratation de la poudre de verre activée et de la poudre de verre dans le ciment. Le model de modifié, appelé le "MOD-modèle" est également utilisé pour prédire les types, les compositions et les quantités de produits de réaction. En outre, les données d'hydratation de la poudre de verre, obtenues à titre expérimental, sont intégrées dans le MOD-modèle pour déterminer l'effet de l'ajout de la poudre de verre sur le processus d'hydratation et les propriétés du pâte de ciment. Les comparaisons entre la théorie et les résultats expérimentaux sont faites pour évaluer les modèles développés. Les prévisions du MOD-modèle ont été validées en utilisant les résultats expérimentaux, et ont été utilisées par la suite pour vérifier plusieurs propriétés de la pâte de ciment avec la poudre de verre hydratée. Ces propriétés comprennent, par exemple, le CH contenu dans la pâte, la porosité, le degré d'hydratation de la poudre de verre et le contenu du CSH ordinaire et du PV-CSH. Les résultats montrent que le MOD-modèle est capable de simuler avec précision les processus d'hydratation de la pâte de ciment mélangée avec de la poudre de verre et peut être utilisé pour prédire diverses propriétés de la pâte hydratée.

Mot-clé : déchets; poudre de verre; l'hydroxyde de calcium; matériau pouzzolanique; l'hydratation du ciment; CEMHYD3D, simulation.
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Finally, I present my angel, Nour, with this success. With her, I was given the most precious feelings in the world, the feelings of a mother.
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<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-S-H</td>
<td>Calcium silicate hydrate</td>
</tr>
<tr>
<td>C</td>
<td>Calcium oxide (CaO)</td>
</tr>
<tr>
<td>S</td>
<td>Silicon dioxide (SiO₂)</td>
</tr>
<tr>
<td>H</td>
<td>Water (H₂O)</td>
</tr>
<tr>
<td>A</td>
<td>Aluminium oxide (Al₂O₃)</td>
</tr>
<tr>
<td>F</td>
<td>Ferric oxide (Fe₂O₃)</td>
</tr>
<tr>
<td>Š</td>
<td>Sulphate oxide (SO₃)</td>
</tr>
<tr>
<td>Ca/Si</td>
<td>Calcium to silicon ratio</td>
</tr>
<tr>
<td>w/s</td>
<td>Water to solid (cement + mineral admixture) Ratio</td>
</tr>
<tr>
<td>Q</td>
<td>Connectivity coefficient</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimension</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimension</td>
</tr>
<tr>
<td>CA</td>
<td>Cellular automata rules</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>CH</td>
<td>Calcium hydroxide</td>
</tr>
<tr>
<td>C₃S</td>
<td>Tricalcium silicate</td>
</tr>
<tr>
<td>C₂S</td>
<td>Dicalcium silicate</td>
</tr>
<tr>
<td>C₃A</td>
<td>Tricalcium aluminate</td>
</tr>
</tbody>
</table>
C₄AF : Tetracalcium aluminoferrite
C₃A•3CSH₃₂ : Ettringite
C₃A•CSH₁₂ : Sulfo-aluminate hydrate
Q₀ : Monomer
Q₁ : Dimer
Q₂ : Pentamer
ASR : alkali silica reaction
GP : Glass powder
PGP : Pozzolanic glass powder
RGS : reactive glass sand
w/c : Water to cement Ratio
D.O.H : Degree of hydration
f : Initial volume fraction of cement
f(0) : Volume fraction of C₃S in the system in the beginning at the dissolution process
f(m) : Volume fraction of C₃S remaining in the system after m cycles of hydration
Vₚ₀ : Pore volume
ϕ : Diameter of the capillary pore
ϕ₀ : Minimum capillary pore diameter
a : Pore structure constant.
molrv : Molar volume of C-S-H
T : Temperature
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{i}^{G} )</td>
<td>Number of moles of oxide ( i ) in glass powder</td>
</tr>
<tr>
<td>( m^{G} )</td>
<td>Mass of glass powder</td>
</tr>
<tr>
<td>( M^{GP} )</td>
<td>Molar mass of glass powder</td>
</tr>
<tr>
<td>( y_{i} )</td>
<td>Molar fraction of oxide ( i ) in glass powder</td>
</tr>
<tr>
<td>( x_{i}^{G} )</td>
<td>Mass fraction of oxide ( i ) in glass powder</td>
</tr>
<tr>
<td>( n_{pu}^{G} )</td>
<td>Moles of alkalis in the pore solution</td>
</tr>
<tr>
<td>( n_{H} )</td>
<td>Moles of water required for the reaction</td>
</tr>
<tr>
<td>( n_{C-S-H} )</td>
<td>Moles of the hydration product C-S-H</td>
</tr>
<tr>
<td>( n_{HT} )</td>
<td>Moles of the hydration product hydrotalcite.</td>
</tr>
<tr>
<td>( n_{CH} )</td>
<td>Moles of CH</td>
</tr>
<tr>
<td>C_{(S_{a},N_{1.1})}</td>
<td>Glass powder formula</td>
</tr>
<tr>
<td>GP C-S-H</td>
<td>Glass powder calcium silicate hydrate</td>
</tr>
<tr>
<td>( n_{i} )</td>
<td>Moles of alkali ions (K+ or Na+) in cement</td>
</tr>
<tr>
<td>( n_{i}^{cement} )</td>
<td>Moles of alkali ions in cement sulfates</td>
</tr>
<tr>
<td>( f_{i}^{w} )</td>
<td>Mass fraction of the alkali oxide ( i ) in the sulfate</td>
</tr>
<tr>
<td>( n_{s}^{T} )</td>
<td>Moles of sulfate in clinker</td>
</tr>
<tr>
<td>( n_{i}^{B} )</td>
<td>Moles of the alkali ions bound in the hydration product</td>
</tr>
<tr>
<td>( n_{i}^{p} )</td>
<td>Amount of alkali ions in the pore solution</td>
</tr>
<tr>
<td>( C_{i} )</td>
<td>Concentration of the alkali ions ( i ) (mol/L)</td>
</tr>
<tr>
<td>( V_{w} )</td>
<td>Volume of the pore solution</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$m_{c-S-H}$</td>
<td>Mass of the C-S-H in the solids</td>
</tr>
<tr>
<td>$n_{Al}^{TP}$</td>
<td>Amount of alkalis in the portland cement</td>
</tr>
<tr>
<td>$n_{Al}^{GC}$</td>
<td>Moles of alkalis released from glass powder</td>
</tr>
<tr>
<td>$n_{Al}^{TG}$</td>
<td>Total amount of alkalis in the glass powder</td>
</tr>
<tr>
<td>$m_{c-S-H}^G$</td>
<td>Mass of C-S-H produced due to the glass powder hydration</td>
</tr>
<tr>
<td>NBO</td>
<td>Non-bridging oxygen atoms</td>
</tr>
<tr>
<td>$V_c$</td>
<td>Number of Pixels of Cement</td>
</tr>
<tr>
<td>$V_{GP}$</td>
<td>Number of pixels of glass powder</td>
</tr>
<tr>
<td>$V_w$</td>
<td>Number of pixels of water</td>
</tr>
<tr>
<td>$SH_{ch}$</td>
<td>Chemical shrinkage of the paste (ml/gm-cement)</td>
</tr>
<tr>
<td>$W_{paste}$</td>
<td>Paste weight (gm)</td>
</tr>
<tr>
<td>MOD</td>
<td>The Modification of the old model</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 General

Nowadays, concrete is considered, all over the world, the most widely used construction and building material due to many advantages of its use. These advantages include the relatively low cost, high durability and ease of forming in different shapes. However, concrete has some disadvantages such as low tensile strength, high internal microcracking, high weight/strength ratio and vulnerability to time-dependent volume changes such as shrinkage and creep. Hence, it is vitally important to work on reducing these disadvantages for a better use of such an important construction material.

Concrete consists of two main materials: cement paste and aggregate. In addition, the transition zone between the cement paste and the aggregate mostly affects the concrete properties, particularly, for normal and low strength types of concrete. The concrete properties are affected by those of the cement paste, which consists of hydrated cement and pores. The microstructure of the cement paste is actually based on the cement hydration process, which is the reaction of cement with water. Hence, it is very important to study and analyze the cement hydration process as a first step for improving the properties of concrete.

Most of the chemical, physical and mechanical properties of concrete are attributed to the cement hydration process. These properties include shrinkage, conductivity, pore solution alkalinity, compressive strength, tensile strength and durability. All of these properties
depend on the nature and the microstructure of the cement paste composition. Hence improving the concrete industry is directly linked to a good understanding of the cement hydration process.

Adding pozzolanic materials to enhance the cement hydration properties is also deemed an effective solution to improve the concrete characteristics, and hence enrich the concrete industry. These pozzolanic materials, including slag, fly ash and silica fume, proved to have significant effects on the cement paste properties on the long term. These additives are often waste materials, which, if not properly employed, will cause environmental problems; hence recycling these materials by reusing them in the construction industry, particularly in the concrete industry, directly benefit the environment by decreasing pollution. This, in fact, adds to the many aforementioned advantages of using pozzolanic additive materials.

As a result of the effects of such additives on the final concrete product, new pozzolanic materials can be used to further enhance the concrete characteristics. In the current work, glass powder as a waste material is examined to be used in enhancing the characteristics of concrete on the basis that it is one of the pozzolanic materials. The experiments in this research work have been carried out primarily to prove that glass powder belongs to the pozzolanic materials “family”.

1.2 Glass Powder

The reuse of waste glass poses a major problem in large municipal areas in North America. Glass is produced in many forms, including packaging or container glass (bottles and jars), flat glass (windows and windscreens), bulb glass (light globes) and cathode ray tube glass (TV screens, monitors, etc.), with different limited service life due to its production purpose. These waste glass types need to be reused and recycled to avoid environmental problems that would be created if they were to be stockpiled or sent to landfills. Post-consumer glass is often mixed-colour and blended with plastics and metals, contaminated with other materials like ceramics and organic matters and partially broken. This reduces its value and complicates the ability to achieve the cullet specifications of bottle manufacturers or other markets such as the construction industry.
Many recycling operations realize that they gain little - or even have a loss of - income by processing glass. Closed-loop recycling, the process of collecting, sorting, transporting, beneficiating, and manufacturing glass back into bottles, is the most common form of glass recycling and has costs embedded in each step of the process. Because the glass is of mixed-colour, and much of it is broken, it cannot be easily recovered for closed-loop recycling. The disposal of the mixed broken glass as a residue from the recycling process causes a significant cost to recyclers (Meyer et al., 2001). In the past, alternative solutions for disposing mixed-colour glass have been sought, but none of these have proven to be successful in an economic sense. In addition, environmental problems would be created if this valuable resource is simply wasted or underutilized, while using up increasingly scarce landfill capacity.

The use of recycled materials in construction is among the most attractive options to consume these wastes without affecting the environment. The main applications include partial aggregate replacement in asphalt concrete, the use as fine aggregate in pipe bedding, landfill gas venting systems and gravel backfill for drains (Chesner et al., 1997). The use of recycled glass in concrete opens a vast new market for mixed as well as colour-sorted broken glass in a variety of specialty products or in local concrete operations. Recent research findings will make it possible to utilize glass also in regular concrete applications, thereby expanding and developing markets for recycled glass. By grinding the waste glass into small pieces, it can be used in concrete. Based on the degree of grinding of the waste glass, it can be used as course aggregate, fine aggregate, fine filler or mineral admixture in concrete. Meyer et al., 1996, investigated the use of mixed waste glasses as aggregates in cement concrete and they concluded that concrete with waste glasses always cracks.

Very limited research work has been conducted on the use of waste glass powder as a cement replacement in concrete (Shao et al., 2000 and Dyer et al., 2001). Recently, few researchers have attempted the use of the glass as raw siliceous materials for the production of Portland cement (Chen et al., 2002 and Xie et al., 2002). There is a clear gap in the research work on the use of glass powder as cement replacement in concrete. Our interest in this work is to study the effect of the recycled glass (glass powder) as a mineral admixture on
the properties of cement paste. Studying its reaction as a pozzolanic material inside the cement hydration matrix is also one of our research objectives.

1.3 Computer Modelling

Computer modelling of the cement hydration process provides the possibilities to bridge the gap between the overall objective of the material and the observed individual facts on it. The modelling is a theoretical and mathematical representation to predict experimental observations (Jennings et al., 1996). Hence, experimental results can be predicted by modelling work, which can deepen the understanding of the material and extrapolate properties outside the available data. The main goal of the microstructural modelling is to predict the performance of cement-based materials throughout their service life.

Computer simulations are required for describing the chemical and physical characteristics of the cement hydration process, which is complicated due to several factors affecting its execution. The cement paste is the most important component affecting the concrete strength due to the internal bond of the Calcium Silicate Hydrate (C-S-H) which is a cement hydration product. The structure of C-S-H is not unique and depends on many factors that affect its internal bond. These factors include the water/cement ratio, cement composition, time, etc. There is a lack of research work related to the mathematical modelling of the cement hydration process. These mathematical models are required to create a complete simulation of the hydration process starting from the contact between water and cement until the hardening of the cement paste. The few available computer models, which describe the hydration process of the Portland cement, are actually based on the huge available experimental data on the hydration of Portland cement.

Bentz (1997, 2000 and 2005) created a complete computer program model CEMHYD3D that simulates the cement hydration process. Although the model results gave a good agreement with the experimental results, some improvements are necessary to be implemented in the existing model to include its ability to determine the cement hydration properties numerically. The properties of the produced concrete can then be controlled by means of limiting the different parameters affecting the hydration process, identified
numerically. Moreover, there is a clear lack in modelling glass powder cement reaction. At least three reasons prevent the execution of glass powder blended cement modelling: (a) the lack of knowledge about the chemistry of the glass powder reaction; (b) the complexity involved with the interaction between the two constituents in glass powder cement (glass powder and Portland cement); and (c) the reactivity of glass powder in cement. The glass powder blended cement can be simulated numerically if the reaction behaviour of the glass powder in the blended cement is revealed based on experiments, which is one of the objectives of this work. To use the glass powder in cement, it is important to know its influence on the cement paste behaviour in both the short and long terms. So, a huge amount of experiments are required to test the glass powder blended cement paste behaviour with time. There is much less information on the reaction of the glass powder in the cement due to the many factors affecting the reaction. Modelling the glass powder in cement, taking into account the different factors affecting the reaction, can simulate the hydration and microstructure development of the glass powder blended cement paste and predicting the long term evolution properties.

This research also includes modelling the glass powder cement hydration. The simulation results of the models can be used for further applications. For example, the reactivity of the glass powder can be derived from the glass powder hydration degree, which in turn can be used to assess the performance of the glass powder. The resultant microstructure, containing information about the cement hydration products and the anhydrous cement can be used for predicting the long term performance of concrete such as strength, durability and volume change.

1.4 Objectives

The work presented in this thesis involves fundamental knowledge of cement chemistry, new development in computer science and practical experience in concrete technology. Experiments carried out in this thesis are used to validate the theoretical derivations and models. These theories are further implemented into a 3D computer based model ready to use in a scientific or industrial environment.
It is always kept in mind that this work should not only contribute to fundamental knowledge about concrete chemistry, but also address practical questions encountered in engineering and to develop new numerical tools for the application of glass powder in cement. Four main objectives are dealt with in this research work; these include:

1. Investigating experimentally the reaction of the glass powder with calcium hydroxide CH and water and determining the consumption of the water and CH with time. The reactivity of glass powder with respect to the oxide composition of glass powder itself and the alkalinity of its environment are also investigated using different activators such as temperature or alkalis.

2. To experimentally study the reactivity, degree of hydration, and the pore solution nature of the glass powder blended cement. The effect of adding different ratios of glass powder on cement hydration is also investigated.

3. To develop 3D computer-based models to simulate the chemical reaction of the activated glass powder hydration and glass powder in cement, to predict the types, compositions and quantities of reaction products and other related quantities such as water retention, chemical shrinkage and porosity of the hydrated matrix.

4. To model the hydration of the glass powder based on its reaction information obtained experimentally. The glass powder hydration information can be incorporated in the cement hydration computer model such as CEMHYD3D model, (Bentz, 1997) to determine the effect of adding glass powder on the cement hydration process and the cement paste properties. Comparisons between the theoretical and experimental results will be made to evaluate the developed models.

1.5 Outline of Thesis

This thesis consists of 7 chapters, which are described below in detail.

Chapter 1, gives an introduction to the thesis and summarizes the objectives of the work.

Chapter 2 presents a literature review, which contains some background on Portland cement composition, cement hydration and cement hydration products. A review of
previous work on the microstructural characteristics of the hydrated cement is also included in Chapter 2. Previous work on using the glass powder in the concrete industry is also discussed. Some of the computer models simulating the hydration process of Portland cement are introduced. A detailed discussion of the CEMHYD3D model is presented. This body of knowledge is expected to provide the basis for understanding the prospective development in this thesis.

**Chapter 3** introduces glass powder as a new material investigating its composition and microstructure. Theoretical models simulating the activated-glass powder reaction are also proposed in Chapter 3. Details of the experiments carried out to determine the characteristics of the activated-glass powder reaction such as water and CH consumption, pH and its reactivity are also presented in Chapter 3.

In **Chapter 4**, an investigation of the glass powder blended cement is presented. Interactions between the reaction of pure glass powder and those of the clinker phases are investigated based on concepts such as product equilibrium and CH consumption. Results of the experiments carried out to investigate the behaviour of the glass powder inside the cement hydration matrix are presented. Models developed to simulate the reaction of the glass powder in cement are also presented.

**Chapter 5** focuses on the computer modelling of glass powder blended cement hydration. Detailed explanations of the CEMHYD3D model assumptions, model techniques, different simulation methods and the nature of the inputs and outputs are also presented. Modifications of the CEMHYD3D model, developed for simulating the glass powder blended cement hydration making use of the new theoretical models proposed in Chapters 3 and 4, are also discussed.

**Chapter 6** is concerned with the comparisons between the theoretical results of the modified CEMHYD3D model and the experimental results carried out in the laboratory for this purpose. These experiments are used to evaluate the proposed model outputs of the glass powder blended cement hydration.
Finally **Chapter 7** includes conclusions of this research. Furthermore, this chapter gives recommendations of the use of the theories, computer models and the use of glass powder in the concrete industry.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter reviews four different main topics, which are:

1- the hydration and microstructure of Portland cement,
2- the previous work of using glass powder in concrete,
3- cement hydration modelling and quick review of the different existing models, and
4- a detailed discussion of the CEMHYD3D model.

The composition, hydration and hydration products of Portland cement are discussed according to the previous work. The different theories describing the Portland cement hydration process are also discussed. Glass powder is a new material used in the concrete industry. Hence, few works have been carried out to describe the concrete behaviour with glass powder. Some concrete mechanical properties, due to the addition of the glass powder, are studied. The CEMHYD3D model is discussed in detail as a complete computer model that describes the hydration process for different types of Portland cement. This model will be modified afterwards to include the hydration of the glass powder inside the cement hydration matrix.
2.2 Hydration and Microstructure of Portland Cement

2.2.1 Portland Cement Composition

ASTM C 150 (2005) defines Portland cement as "a hydraulic cement produced by pulverizing clinkers consisting essentially of hydraulic calcium silicates, calcium aluminates, ferrite and usually containing one or more of the forms of calcium sulfate as an inter ground addition". In addition, there can be some minor oxides as a result of the cement manufacturing due to the presence of some impurities in the raw material composition.

The clinker has a composition of 67% CaO, 22% SiO₂, 5% Al₂O₃, 3% Fe₂O₃ and 3% other products (Taylor 1997). All of these components composed together form the main cement phases; namely, alite, belite, aluminate and ferrite, which react with water to contain hydrated cement products. The phase compositions in Portland cement are denoted by ASTM as tricalcium silicate (C₃S), dicalcium silicate (C₂S), tricalcium aluminate (C₃A), and tetracalcium aluminoferrite (C₄AF) (Stein et al., 1964). In the clinker, minor phases in addition to the four principal phases can be found. Most significant of these are the magnesium oxides MgO, alkalis in the form of Na₂O, K₂O and the sulfates SO₃ (Taylor 1997). In addition, calcium sulfate is a retarder used to delay the setting time of cement paste during the hydration process with approximately 5% of calcium sulfate. There are different compositions of calcium sulfate which are gypsum (CaSO₄•2H₂O), hemihydrates (CaSO₄•0.5H₂O) and anhydrite (CaSO₄). At 40°C under dry conditions, gypsum (CaSO₄•2H₂O) slowly dehydrates to hemihydrate (CaSO₄•0.5H₂O) or anhydrite (CaSO₄) (Wang et al., 2004).

Portland cement may be blended with glassy cementitious materials to form blended hydraulic cements. The most common glass cementitious materials used are fly ash and silica fume as pozzolans and blast furnace slag (Demirboga 2003).

2.2.2 Cement Hydration

Cement is a complex mixture. Many studies have explained the hydration chemistry of cement constituent phases. For a given particle size and w/c ratio, X-ray diffraction analysis
(X-R-D) showed that maybe 70% of the C₃S reacts in 28 days and virtually all in one year (Taylor 1997).

2.2.2.1 Tricalcium Silicate Hydration

The reaction of C₃S with water is represented as follows:

\[
2\text{C}_3\text{S} + 7\text{H} \rightarrow \text{C}_3\cdot\text{S}_2\cdot\text{H}_4 + 3\text{CH} \\
\downarrow \quad \downarrow \\
\text{C-S-H} \quad \text{CH}
\]

\[\text{Eq. 2.1}\]

The formula for calcium silicate hydrate C-S-H in the above equations is somewhat approximate because there is no certain composition for C-S-H due to the differences of calcium/silicon (Ca/Si) and water/solid (w/s) ratios, in the C-S-H structure, with time.

2.2.2.2 Dicalcium Silicate Hydration

The hydration of dicalcium silicate phase can be represented by the equation.

\[
2\text{C}_3\text{S} + \text{SH} \rightarrow \text{C}_3\cdot\text{S}_2\cdot\text{H}_4 + \text{CH} \\
\downarrow \quad \downarrow \\
\text{C-S-H} \quad \text{CH}
\]

\[\text{Eq. 2.2}\]

The amount of Ca(OH)₂, (CH) formed in this reaction is less than that produced in the hydration of C₃S. The hydration of C₃S is much slower than the C₃S hydration. C₃S is more reactive than C₂S due to the difference in the amount and arrangement of calcium atoms in the structure of the two phases, which may affect the degree of hydration of the two phases (Ramachandran et al., 2001).

2.2.2.3 Tricalcium Aluminate Hydration

Tricalcium aluminate reacts with water to form C₂AH₈ and C₄AH₁₃ of hexagonal phases. These products are unstable thermodynamically and convert to the C₃AH₆ phase of the cubic phase immediately in the absence of any stabilizing admixtures. The relevant equations for these reactions are:
The cubic form (C₃AH₆) can also form directly by hydrating C₃A at temperatures of 80°C or above (Ramachandran et al., 1973).

\[ 2C_3A + 21H \rightarrow C_3AH_{13} + C_2AH_8 \]  \hspace{1cm} \text{Eq. 2.3}

\[ C_3AH_{13} + C_2AH_8 \rightarrow 2C_2AH_6 + 9H \]  \hspace{1cm} \text{Eq. 2.4}

The C₃A hydration is mainly responsible for releasing a great amount of heat in the initial few minutes of the cement hydration process to cause a flash set for the paste. In Portland cement, to avoid the flash set, the hydration of the C₃A phase is controlled by the addition of gypsum. The C₃A phase reacts with gypsum in a few minutes to form ettringite as follows:

\[ C_3A + 6H \rightarrow C_3AH \]  \hspace{1cm} \text{Eq. 2.5}

\[ C_3A + 3C\text{SH}_2 + 26H \rightarrow C_3A\cdot3C\text{SH}_{12} \]  \hspace{1cm} \text{Eq. 2.6}

After all the gypsum is converted to ettringite, the excess C₃A will react with ettringite to form the low sulfo-aluminate hydrate; i.e.

\[ C_3A\cdot3C\text{SH}_{12} + 2C_3A + 4H \rightarrow 3[C_3A\cdotC\text{SH}_{12}] \]  \hspace{1cm} \text{Eq. 2.7}

When the entire sulfate is consumed, the ettringite reacts with C₃A resulting in the formation of monosulfo-aluminate hydrate. This conversion will occur in cements within 12–36 hrs with an exothermic peak. The addition of some admixtures may accelerate or delay this conversion (Beaudoin et al., 1992).

2.2.2.4 Ferrite Hydration

The C₄AF phase hydration has the same sequence of products as that of C₃A, however, the reactions are slower. In the presence of water, C₄AF reacts as follows:

\[ C_4AF + 16H \rightarrow 2C_2(A,F)H_8 \]  \hspace{1cm} \text{Eq. 2.8}

\[ C_4AF + 16H \rightarrow C_4(A,F)H_{12} + (A,F)H_3 \]  \hspace{1cm} \text{Eq. 2.9}
Amorphous hydroxides of Fe and Al form in the reaction of C₄AF. The thermodynamically stable product is C₃(Al,F)H₆ and this is the conversion product of the hexagonal hydrates. C₄AF reacts much slower than C₃A in the presence of gypsum. In other words, gypsum retards the hydration of C₄AF more efficiently than does C₃A (Young 1981). The reaction of C₄AF with gypsum is as follows:

\[
3\text{C}_4\text{AF} + 12\text{CSH}_2 + 110\text{H} \rightarrow 4[\text{C}_6(\text{Al,F}) \text{SH}_{12}] + 2(\text{Al,F})\text{H}_3
\]

Eq. 2.10

The low sulfo-aluminate phase can form by the reaction of excess C₄AF with the high sulfoaluminate phase. That is,

\[
3\text{C}_4\text{AF} + 2[\text{C}_6(\text{Al,F}) \text{SH}_{12}] \rightarrow 6[\text{C}_6(\text{Al,F}) \text{SH}_{12}] + 2(\text{Al,F})\text{H}_3
\]

Eq. 2.11

At low w/c ratios and high temperatures the low sulfoaluminate may form directly (Ramachandran et al., 1980).

2.2.3 Hydration Theories and Kinetics

Cement is a complex mixture. Many studies have explained the hydration chemistry of cement constituent phases. For a given particle size and w/c ratio, XRD showed that maybe 70% of the C₃S reacts in 28 days and virtually all in one year, Taylor (1997). The products of reaction are crystalline calcium hydrate (CH) and amorphous calcium silicate hydrate C-S-H. Also βC₂S has the same reactivity results as C₃S but in a slow rate of hydration. About 30% of βC₂S reacts in 28 days and 90% in one year. The evaluation of hydrating cement can be characterized by the heat evolution curve which is shown in Figure (2.1). There are five stages in the hydration of plain cement described as follows by Bentz et al. (1994):

- **Pre-induction:** This is the initial rapid hydration that occurs when the particles of cement are mixed with water, releasing a large amount of heat. Its duration does not exceed a few minutes.
- **Induction:** A period of reduced hydration activity. Many theories have been proposed. Its duration is about 1-2 hours.
- **Acceleration:** The rate of hydration increases. This is the beginning of the setting of the cement paste. Its duration does not exceed a few hours.
• Deceleration: The hydration rate decreases as the hydrated material covers the particles. Its duration is in the order of hours to days.

• Limited diffusion: Hydration and aggregation occur at a very low rate. Reactions are limited by the rate of diffusion of the species through the dense paste. Its duration is in the order of days to years.

In the induction period, which occurs while the consistency of the cement remains constant, the hydration of C₃S begins and there is heat release due to the reaction. The end of the induction period occurs when the growth of C-S-H begins. The thickening of cement occurs after the induction period finishes, when a secondary growth of C-S-H causes the formation of hydration shells from adjacent grains connected to each other to thicken the cement paste, Preece et al. (2000).

![Figure (2.1): Cement Hydration Stages. Bentz et al. (1994)](image)

There are two theories that attempt to explain the hydration mechanism: protective coating theories and nucleation delay theories. Protective coating theories have two main schools of thought, the first school maintains that C-S-H occurs in numbers of morphological forms; these different types of C-S-H have different permeabilities that control the rate of the cement hydration. It is thought that C-S-H undergoes three phase transformations during the induction period. The permeability of these phases leads to more rapid hydration for C₃S
grains. The level of calcium hydroxide in the solution controls the rate of transition between the three different types of C-S-H. The second protective coating theory is known as the osmotic pressure hypothesis, where it is thought that after mixing cement with water, a thin hydration shell forms at the surface of the grain. As a result of the relative sizes of water and Ca ions, they can diffuse through this shell. By continuing this process, an osmotic pressure builds up because the silica ions cannot escape. The end of the induction period is marked by the rupture of the shell by the osmotic pressure and the formation of secondary C-S-H.

The second mechanism involves a delay in building up of C-S-H. It is thought that the growth of C-S-H on the surface of the grains depends on the concentration of calcium ions in the solution. The solution becomes supersaturated at the end of the induction period containing CH particles, which then precipitates to cause increasing in the rate of formation of C-S-H, cement paste begins to thicken after that, Preece et al. (2000).

2.2.4 Hydration Products

2.2.4.1 C-S-H

C-S-H Nature

Calcium-silicate-hydrate C-S-H, which is formed from the hydration of C₃S or βC₂S is the main component of the hydrated cement products. Its structure is amorphous or poorly crystalline molecules. The early products in the hydration of C₃S consist of foils and flakes. After a few days these products consist of C-S-H fibres and partly crumpled sheets. At later stages of hydration, a dense, mottled C-S-H structure (inner product) is observed in hydrated C₃S. The crystallinity of C-S-H is affected by the temperature. At normal temperatures, the C-S-H phase is represented as an amorphous gel structure; however, at high temperatures, the C-S-H structure can range from poorly-crystalline to crystalline structure (Ramachandran et al., 2001).

The morphology of C-S-H gel particles in the cement paste frame is divided into two types. Type 1 is C-S-H (I), which is found in the form of elongated or fibrous particles. These particles can be described as spines, acicular, aciculae, prismatic, rod-shaped and rolled sheets of a few micrometers long. Type 2 is C-S-H (II); it is described as a reticular or
honeycombed structure with low density and is usually produced at the same time of producing C-S-H (I). There are other two types of C-S-H that can be prepared with a crystalline morphology, which are called tobermorite and jennite types. These types consist of flattened particles (under 1000Å in largest dimension). The morphology of C-S-H (I) is similar to the morphology of the tobermorite type and the morphology of C-S-H (II) is similar to the morphology of the jennite type (Taylor 1997).

**Silicate Anion Structure of C-S-H**

The silicon ion $\text{Si}^{4+}$ has four free protons, each proton is attracted by one electron of oxygen ion $\text{O}^{2-}$, thus the silica atom connects with four oxygen atoms to form a deierketten chain layer. But every oxygen atom has two electrons, one of them attracts a proton from the silicate atom and the other attracts either a hydrogen atom to form silicate hydroxide chain, or a $\frac{1}{2}$ Ca atom to form Ca-O layers, as shown in Figure (2.2) (Richardson 2004).

There are Ca$^{+2}$ ions and water molecules in the interlayer of the structure of C-S-H (Ramachandran et al., 1981). The existence of water molecules within the C-S-H matrix can enhance the modulus of elasticity of the body or it can compensate for any decrease in the Young's modulus when the layers of C-S-H move apart. Both Si-OH and Ca-OH bonds occur in C-S-H, Si-OH decreases and the Ca-OH bond increases by increasing the Ca/Si ratio (Cong et al., 1996).

![Figure (2.2): The Structure of the Dimer Silicate Chain (Richardson 2004).](image)
There are five terms referring to the connectivities. Q0 is a single tetrahedra (monomer) thus denoting isolated tetrahedra, Q1 is the end group tetrahedra in which a tetrahedron connects with only another tetrahedron (dimer), Q2 is a middle group tetrahedra (pentamer), which is a tetrahedron connecting with two other tetrahedra and so on for Q3 and Q4. For C₆S or β-C₂S, the content of Q0 begins to decrease after few hours, with formation of Q1, later accompanied by Q2; no Q3 or Q4 is detected. Figure (2.3) illustrates the connectivities of Q1 and Q2 according to Richardson 1999.

The chain length contains 2, 5, 8, ...., (3n-1) tetrahedra, which is an integer number (Taylor, 1986). Sometimes in the bridging tetrahedra, Al³⁺ ions replace Si⁴⁺ ions in the C-S-H gel. The amount of Al³⁺ in the bridging chain does not exceed 0.1 of the amount of Si⁴⁺ atoms. Taylor (1986) concluded that the Ca/Si ratio decreases with an increase in the chain length. For tobermorite and jennite at early ages, the dimeric tetrahedra chains are formed with the Ca/Si ratios equal to 1.2 and 2.3 respectively. By the time the dimeric chains convert to a more polymeric order, especially pentamer (Si₅O₁₆H), with an infinite chain length, then the Ca/Si ratio decreases to 0.8 and 1.6 for the tobermorite and jennite, respectively.

Figure (2.3): The Connectivity of the Dreierketten Chain (Richardson 1999)
2.2.4.2 Ca(OH)$_2$

In a fully hydrated Portland cement, Ca(OH)$_2$ constitutes about 20–25% of the solid content from the C$_3$S and $\beta$C$_2$S phases of hydration. The crystals are plate-like or prismatic and cleave readily. They may be produced at the same time as the production of C-S-H. The density of Ca(OH)$_2$ is 2.24 g/cm$^3$. The crystalline Ca(OH)$_2$ gives sharp XRD patterns. The morphology of Ca(OH)$_2$ may vary and form as equidimensional crystals, large flat plate-like crystals, large thin elongated crystals, or a combination of them.

2.2.4.3 Ettringite (AFt phases)

The ettringite is called the AFt phase in cement paste, depending on Al-Fe-tri (tri = three moles of C$_3$S) of the formula C$_3$A•3C$_5$S•H$_{32}$ in which Al can be replaced by Fe in the case of ferrite hydration. The AFt phase forms in the first few hours (from C$_3$A and C$_4$AF) and its amount plays a role in controlling the setting. After a few days of hydration, only a little amount of it may remain in cement pastes. It appears as short rods in the SEM and the length does not normally exceed a few micrometers (Ramachandran et al., 2001).

2.2.4.4 Monosulfate (AFm phases)

The monosulfate is known as the AFm phase under the C$_4$ASH$_{12}$ or C$_4$A•C$_5$S•H$_{12}$ formula. In Portland cement, this phase form is produced due to the consumption of the AFt phase when it reacts with the C$_4$A or C$_4$AF phases. This phase may constitute about 10% of the solid phase (Ramachandran et al., 2001).

Figure (2.4) shows a Scanning Electron Microscope SEM image for the different product hydration phases in the cement paste.
2.3 Glass Concrete

2.3.1 Introduction

The commercial production of glass concrete products requires a reliable supply of glass that is cleaned, crushed, and graded according to specifications. The crushing and grading operations ought to be coordinated such as to result in preferably zero wastage. Architects or designers can help coordinate the colours of glass aggregate and cement matrix. Also, the choice of surface texture and treatment may benefit from specialists trained in the visual arts.

The development of an appropriate production technology should recognize the differences between glass and natural aggregates. For example, the basically zero water absorption of glass improves the mix rheology and calls for quite different mix designs, including the choice of admixtures, which depends also on whether a dry or wet technology is used. Since plain Glass Concrete is quite brittle, just like conventional concrete, it is advantageous to reinforce glass concrete products with either randomly distributed short fibres or, in the case of thin sheets or panels, with fibre-mesh or textile reinforcement (Mu et al., 2001).
2.3.2 Glass Powder in Concrete

There is lack of research works investigating glass powder blended cement behaviour. Existing works investigated the behaviour of using different types of glass powder as a partial replacement of either cement or aggregates depending on the glass powder particle size. Some of these works compared the pozzolanic behaviour of glass powder to that of other pozzolanic materials such as fly ash inside the concrete (Shi et al., 2005). Others investigated the compressive strength, durability, aggregate silica reaction and permeability of glass powder concrete. Glass powder concrete has been studied at its microstructural level.

Shayan and Xu (2004) studied the use of waste glass in concrete in several forms, including fine aggregate, coarse aggregate and glass powder. The use of glass powder in concrete would prevent an expansive alkali silica reaction (ASR) in the presence of susceptible aggregate. Release of alkali from GP did not appear to be sufficient to cause deleterious ASR expansion. Microstructural examination has also shown that GP would produce a dense matrix and improve the durability properties of concrete incorporating it. It has been concluded that 30% of GP could be incorporated as cement or aggregate replacement in concrete without any long-term detrimental effects. Up to 50% of both fine and coarse aggregates could also be replaced in concrete of 32-MPa strength grade with acceptable strength development properties.

Shi et al., (2005) concluded that finely ground glass powders exhibited very high pozzolanic activity. The finer the glass powder is, the higher is its pozzolanic activity.

An increase in curing temperature accelerates the activation of pozzolanic activity of both glass powder and coal fly ash. Mortar strength testing results indicated that the curing temperature has a greater influence on the pozzolanic activity of glass powder than on that of fly ash. Results from ASTM C1260 (2001) testing indicated that the replacement of Portland cement with ground glass powder also reduces the ASR-induced expansion.

Karamberi and Moutsatsou (2005) used coloured glass cullet as a cement substitute or as aggregate in cementitious materials. They concluded that green cullet exhibited better results.
concerning pozzolanic activity and compressive strength development followed by flint glass cullet. There is no noticeable effect of the fine ground glass cullet on the ASR expansion.

Shayan and Xu (2006) used glass powder manufactured from mixed colour waste packaging glass comprising soda-lime glass. In order to investigate the performance of GP in concrete under field conditions, a field trial was conducted using a 40 MPa concrete mixture, incorporating various proportions of GP (0%, 20%, and 30%) as cement replacement. It was found that GP reduced the chloride ion penetrability of the concrete, thereby reducing the risk of chloride-induced corrosion of the steel reinforcement in concrete; however this issue needs further electrochemical investigation. It was noted that there is no deleterious ASR expansion in the concrete with GP. This may have arisen because the pozzolanic reaction of GP with cement appeared to enhance the binding of alkali, making it unavailable for reaction with reactive aggregate. It is observed that both GP and glass aggregate can be used together in 40 MPa concrete without any adverse reaction.

Taha and Nounu (2007a) studied the influence of two different mineral admixtures, lithium nitrate LiNO₃ and pozzolanic glass powder GP on the expansion induced by alkali-silica reaction (ASR). The presence of pozzolanic glass powder (PGP) in concrete as cement replacement leads to changes in the concentration of hydroxide ion OH⁻ in the pore solution, which is considered a direct reason in reducing the risk of ASR expansion. Lithium nitrate is chemically classified as an alkali metal and can contribute to the total alkali content of the concrete. In their study, it was shown that lithium nitrate as a concrete chemical admixture can successfully reduce ASR expansion.

Taha and Nounu (2007b) used reactive glass sand RGS and pozzolanic glass powder PGP to investigate if these affect the concrete. They concluded that the presence of RGS in concrete will reduce the consistency of the concrete mix and adhesive bond of the ingredients inside the concrete mix. Therefore, severe bleeding and segregation were observed when natural sand was replaced by waste recycled glass sand, and the plastic properties of the concrete mix undergoes notable changes. The smooth and plane surface of the large recycled glass particles can weaken the bond between the cement paste and the glass particles. The quality of cube made with the same mix was significantly affected by the presence of the RGS and PGP in the concrete.
The inherent cracks in the recycled glass sand particles, resulting from the crushing process of recycled glass in order to reduce the glass particle, can be considered as a source of weakness and can reduce the strength of the concrete. The presence of the RGS in concrete reduces its compaction compared to the control mix. Therefore, the strength of the concrete will be negatively affected. The recycled glass sand can reduce the permeability of the concrete mix and may enhance its durability and restrict the migration of the water and ions inside the concrete matrix. The texture properties of the glass particle can be improved by reducing the size of the particles to a very fine powder.

Chen et al. (2006) tested the compressive strength of specimens with 40 wt.% of electrical grade glass (E-glass) content. It was found that the compressive strength of the specimens was 17%, 27% and 43% higher than that of control specimen at an age of 28, 91 and 365 days, respectively. The addition of E-glass significantly improved the sulfate resistance of concrete according to the results of weight loss and strength reduction. E-glass particles can be used as partial fine aggregate replacement material as well as supplementary binding material depending on its particle size. For particle sizes less than 75µm, amorphous E-glass could possess cementitious capability, which results from the hydration or pozzolanic reaction. The coarser cylindrical glass acts as a potential crack-arrester and inhibits the internal crack propagation.

Based on the properties of hardened concrete, the optimum E-glass content is found to be 40–50 wt.% in their study (Chen et al., 2006). However, the slump decreases as the glass content increases due to the reduction of the fineness modulus, and the use of high-range water reducers is needed to obtain a uniform mix. Compared with the control mix, concrete with E-glass has excellent chloride-ion penetration resistance and no adverse ASR-expansion effect. The use of E-glass particles could reduce the cost of cement and fine aggregate in cementitious mixtures and minimize the environmental impact due to solid waste disposal.

2.4 Cement Microstructural Modelling

During the last three decades, many authors have developed computational models for cement-based materials, which are constitutive models based on mathematical equations.
During the last decade, many models were developed to simulate the properties of cement and its hydration products. Cement hydration modelling has advanced to create computer programs simulating the cement hydration process and the microstructure of its products.

There are two points of view for modelling cement-based materials. The first is based on simulating the chemical microstructure of the main silicate hydration product C-S-H. The choice of the C-S-H was made due to its uncertain morphology, which changes with time based on different factors such as the composition of cement, the w/c ratio, the curing temperature, the degree of hydration, and the presence of the chemical and mineral admixtures. All of these factors can affect the composition, the nanostructure and the morphology of the C-S-H. Computer models for calculating the internal bond intensity between the different atoms in the C-S-H are also proposed.

The second point of view is based on simulating the cement structure and the cement hydration process within computer programs using different computer languages such as FORTRAN and C language to obtain an agreement between the experimental results and model outputs.

### 2.4.1 Modelling of C-S-H Structure

Hamid (1981) proposed a model for describing the structure of the 1.1nm tobermorite which has infinite tetrahedra chains Si₆(O/H)₆ parallel to each other and connected together by calcium atoms. For the tetrahedra chain Si₆(O/H)₆, the Si—O bond distance is 1.62Å and the O—O distance is 2.64Å. The Ca₁, Ca₂, Ca₃ and Ca₄ atoms are coordinated with seven oxygen atoms which are four in-plane oxygen atoms O₅, O₂, O₁₁ and O₁₂, two oxygen atoms O₆ and O₃ above or below the calcium atom and the seventh oxygen atom OH₉ above or below the in-plane oxygen atoms forming a tetragonal pyramid. This structure can be seen in Figure (2.5). Also formulas for describing the composition of 11Å tobermorite for various Ca/Si ratios are proposed as follows:

\[
\text{Ca}_4[\text{Si}_6\text{O}_{16}(\text{OH})_6]\cdot\text{H}_2\text{O} \quad \text{for } \text{Ca/Si} = 0.667 \quad \text{Eq. 2.12}
\]

\[
\text{Ca}_5[\text{Si}_6\text{O}_{16}(\text{OH})_6]\cdot2\text{H}_2\text{O} \quad \text{for } \text{Ca/Si} = 0.83 \quad \text{Eq. 2.13}
\]
\( \text{Ca}_4[\text{Si}_4\text{O}_{12}] \cdot 2\text{H}_2\text{O} \) \quad \text{for Ca/Si = 1.0} \quad \text{Eq. 2.14}

The average formula obtained for all Ca/Si ratios is:

\( \text{Ca}_{4x}[\text{Si}_{4x}\text{O}_{13}(\text{OH})_x] \cdot 2\text{H}_2\text{O} \) \quad \text{Eq. 2.15}

Faucon et al. (1996) calculated the potential energy for a pair of atoms \( i-j \) separated by a distance \( r_{ij} \) using the Born-Mayer-Huggin types of potentials, which were used to model the Si-Si, Si-O, Si-Ca, Si-H, O-O, O-Ca, O-H and Ca-Ca interactions. This potential energy is given by Eq. 2.16.

\[
\Phi(r_{ij}) = \Lambda_{ij} \exp \left( \frac{r_{ij}}{\rho_{ij}} \right) + \frac{q_i q_j}{4\pi\varepsilon r_{ij}} \text{erfc} \left( \frac{r_{ij}}{\alpha} \right)
\]

\text{Eq. 2.16}

where \( \Lambda_{ij} \) and \( \rho_{ij} \) are empirical values that depend on the interaction between the pair of atoms used, \( \text{erfc} \) function express the Coulombic interaction and the parameter \( \alpha \) regulates the range of the interaction. The atomic charges used for the Coulombic interactions are formal (Si\(^{+4}\), O\(^{-2}\), Ca\(^{+2}\), H\(^{+}\)). Two other potential energy formulas are investigated to represent the interaction of three atoms; they were applied to the angles O-Si-O, Si-O-Si, Si-O-H and H-O-H, and the \( \text{H}_2\text{O} \) molecules and their possible dissociation into one H\(^{+}\) and one OH\(^{-}\). The atomic positions in the initial cell which are proposed by Hamid (1981) for 1.1nm tobermorite found that there are hydrogen atoms placed randomly at about 0.1nm from the OH and \( \text{H}_2\text{O} \). The structure of the 1.1nm tobermorite using the orthorhombic cell, which was presented by Hamid (1981) is shown in Figure (2.5). For the structure with Ca/Si = 0.83, the calcium atoms were introduced into the labile layer. This parallelepiped simulation cell contains the entire number of orthorhombic cells of tobermorite, and is repeated to infinity by periodic conditions.
2.4.2 Cement Hydration Modelling

Mathematical models have been developed to provide information about the cement hydration process and the microstructure of its hydration products. This information is distributed into two kinds of results: fundamental results such as mass or volume fractions of phases in the paste, cumulative heat evaluation and the physical properties such as strength, porosity and permeability, and non-fundamental results which are based on the simulation of the developing microstructure at the level of individual particles or regions of anhydrous phases (Taylor 1997).

A two-dimensional (2D) finite element modelling has been used to simulate the elastic properties of concrete by Roelfstra et al. (1985). Simulation techniques were used to generate realistic aggregates in two dimensional phases. The model treated the cement paste microstructure as a continuum. This finite element model can compute the elastic moduli, diffusion coefficients and thermal expansion coefficients of the concrete. Tennings et al. (1986) proposed a three-dimensional (3D) model for simulating the C₃S paste microstructure. The model simulated C₃S particles as spheres with a particle distribution size
typical of Portland cement. The model starts by representing the w/c ratio in a successive iteration to calculate the process of the phase changes due to the hydration process in small increments using an algorithm for consuming C₃S and generating the hydration products.

Xi et al. (1996) developed a continuum model to create a computer simulation for the cement microstructure based on the mosaic method. The 2D space set is divided by intersecting lines to result polygonal shapes. These polygonal shapes represent the unhydrated and hydrated cement particles and the cement hydration products. The theoretical relationships of the mosaic model parameters and the material parameters of cement paste are formulated. The model predicts some material parameters such as the w/c ratio, degree of hydration at any age, particle size distribution and density of cement particles.

Navi and Pignat (1996) developed a 3D computer model for simulating the hydration and microstructure development of C₃S pastes classified as the “Integrated Particle Kinetics Model”. The hydrated C₃S turns into products C-S-H and CH. The C-S-H grows inward or outward from the original particle edge, classified as the “inner” and “outer” C-S-H accordingly. CH crystals are produced outside the outer products in the pore space. When one cm³ C₃S dissolves, it produces 1.7 cm³ C-S-H and 0.61 cm³ CH. This part of C-S-H is further divided into two parts: 1 cm³ inner C-S-H and 0.7 cm³ outer C-S-H as shown in Figure (2.6). Therefore, there is always a relation between the rate of C-S-H growth inward and that outward. Methods are proposed to determine the growth rate of inner C-S-H, which can in turn determine the rate of the C₃S dissolution as well.
A three dimensional model describing the microstructure of C₃S hydration was developed by Bentz (1991). In this model, the paste was represented by a three dimensional array of pixels [cubic volume elements]. It is assumed that the pores of C₃S, CH and C-S-H phases are filled with water. Initially, the particles of C₃S are described by pixels and modelled as spheres placed in random locations in a 3D box to achieve a desired w/c ratio. The hydration process is presented in three steps which are: dissolution, diffusion and reaction steps. These steps are shown in Figure (2.7) of a two dimensional description. The first step is that when (n) number of C₃S pixels dissolves due to the existence of water, (n) number of C-S-H diffusing species, 0.7(n) number of extra C-S-H diffusing species and 0.61(n) number of CH diffusing species are produced. These diffusing species exist in a random way in the solution, when diffusing C-S-H meets a surface of C₃S or solid C-S-H pixels, it sticks on it to form more solid C-S-H. Also for the CH diffusing species, it can remain in the pore solution or stick to a solid CH surface existing in the solution, resulting in a growth of the CH crystals. When all diffusing species generated by a given dissolution have reacted, a new hydration cycle is begun by performing another dissolution step. The model gives Equations 2.17 and 2.18 to calculate the w/c and (D.O.H) degree of hydration as follows:

\[
\text{w/c} = \frac{1 - f}{3.2 f} \quad \text{Eq. 2.17}
\]
where \( f \) is the initial volume fraction of cement, the number 3.2 is the specific gravity of C\(_3\)S, \( f(0) \) is the volume fraction of C\(_3\)S in the system at the beginning of the dissolution process and \( f(m) \) is the volume fraction of C\(_3\)S remaining in the system after \( m \) cycles of hydration.

The model also gives a description for the C-S-H structure with the addition of mineral admixtures such as fly ash and silica fume for a percentage of 10% of cement amount. The model had a good agreement with the experimental observations.

![Diagram of Steps in the Hydration Model (Bentz et al., 1991)](image)

**Figure (2.7): Diagram of Steps in the Hydration Model (Bentz et al., 1991)**

Also, two dimensional models were proposed for the microstructure of C-S-H. These models represented degrees of connectivity much lower than the degrees of connectivity in three dimensional models. Thus, the CH was discontinuous in two dimensional sections.

Breugel (1995) proposed a computer-based simulation model to describe the hydration and microstructure development of cement, called the “HYMOSTRUC model”. The hydration model based on data describes the particle size distribution, the chemical composition of the cement, the water/cement ratio and the reaction temperature. Also, the effect of the physical interactions between hydrated cement particles on the hydration rate of individual cement particles is modelled.

\[
\text{D.O.H} = \frac{f(0) - f(m)}{f(0)} \quad \text{Eq. 2.18}
\]
In this model, the cement particles are distributed in the paste. An arbitrary particle is located in the centre of the cubic computational volume, which called "cell". The cell size depends on the water/cement ratio of the paste and the particle size distribution of the cement. The inter-particle contact during the hydration is affected mainly by the amount of cement in the cell.

The hydration products volume is about twice the volume of the cement in the cell. Some assumptions are proposed to control the hydration model, which are:

- The particles of the same size hydrate at the same time,
- The ratio between the volumes of the hydration products and the reactant decreases with increasing the released temperature, and
- The hydration products precipitate in the close vicinity of the hydrating cement particles.

The expansion and interaction mechanisms are shown in Figure (2.8). When the arbitrary particle contacts with water, it starts to dissolve leading to formation of hydration products. Part of the hydration products are formed inside the original surface of the particle and the other part is formed outside this surface. This process causes an expansion of the particle size making a contact with the other nearby particles. Further hydration of the particle goes along with further expansion and embedding of neighbouring particles. Extra expansion is obtained due to the embedding of other particles. The microstructure development is simulated by this way of this expansion mechanism of continuous expansion and embedding of particles.

The cumulative pore size distribution for the capillary pore water can be described mathematically with the following Eq. 2.19

\[
V_{\text{pore}} = a \ln \left( \frac{\phi}{\phi_0} \right)
\]

\text{Eq. 2.19}

where \( V_{\text{pore}} \) is the pore volume, \( \phi \) the diameter of the capillary pore, \( \phi_0 \) the minimum capillary pore diameter and "\( a \)" a pore structure constant.
The original modelling work was based on a statistical distribution of the particles. In later work, the model has been extended to include randomly distributed particles in a predefined envelope shape, representing an initial cement paste system. The hydration algorithm of the extended HYMOISTRUC3-D model is now applied to the randomly stacked particles, calculating the growth of the particles as hydration proceeds. This forms the basis for the so-called "ribbon" model. The extended model also provides information about the capillary pore structure after hydration of the cement particles through the inverse space that remains from the hydrating cement paste volume. This pore structure is the basis for the moisture transport calculations that determines the movement into the capillary.

![Diagram](image)

**Figure (2.8): Interaction Mechanism for Expanding Particles. Left Part: Free Expansion, Formation of Inner and Outer Product. Right: Embedding of Particles, Several Iteration Steps, Breugel (1995)**

### 2.5 CEMHYD3D Model (Bentz et al., 1994)

#### 2.5.1 Introduction

Bentz et al. (1994) created a computer program of a 3D model to simulate the Portland cement hydration process including the hydration reactions for the major cement phases: $C_3S$, $C_2S$, $C_3A$ and $C_4AF$ in addition to the gypsum in the presence of silica fume as a mineral
admixture. The computer model is based on a set of cellular automata-like rules for the main hydration stages: dissolution, diffusion and reaction. The model operates on 3D images of multi-phase particles generated to match specific characteristics of 2D images of real cements. Iterative applications of series probabilistic rules model the physico-chemical cement hydration for updating the microstructure at any given moment of discretized time based on its current state. Three main sub-programs are developed to serve the main cement hydration program execution. These programs create a 2D SEM image for the cement components, convert the cement phase particles from 2D to 3D computational volume and create a 3D SEM image for the cement particles.

The following sections will describe in detail the operation, inputs and outputs for the CEMHYD3D programs.

2.5.2 Model Assumptions

- A computational volume of 100x100x100 pixels is employed.
- All cement, gypsum and admixtures particles are spherical particles.
- The arrangement of the particles is according to their volume from largest to smallest in the computational volumes in which the small particles fill the spaces between the large particles.
- No overlap between the particles is allowed.
- The particle diameters range from 3 to 35 pixels.
- Periodic boundaries are employed such that a particle that extends outward through one or more faces of the 3D microstructure is completed inward through the opposite faces.
- The particles are totally flocculated.
- The reactions are implemented as a series of cellular automata-like rules.
- The connectivity between the different hydration product phases and between pore spaces can be obtained by percolation theory.
2.5.3 **Cellular Automata**

Cellular Automata CA is basically a discrete computer algorithm that discretizes in space and time and operates on a lattice of sites which are pixels in this model. Each pixel in the lattice behaves as a Boolean processor; CA can simulate the hydration process in terms of dissolution, precipitation, nucleation and diffusion. The CA rules are applied to simulate the development of the cement paste microstructure by iterations to all of the pixels comprising the microstructure. The fact that the state variables are discrete means that the quantities they represent and derived quantities are also discrete (e.g. mass, momentum, velocity, etc.) (Bentz et al., 1993).

2.5.4 **Percolation Theory**

The percolation expresses the degree of connectivity term for the solid and pore phases. For the solid phases, the percolation properties can be calculated by a burning algorithm, which is the simplest way to identify all pixels that are part of a spanning cluster. All pixels of the solid phase are combustible. A fire on one side of the model's cell is allowed to propagate only along these combustible pixels. For pore space percolation, at a given w/c ratio, the pore space connectivity decreases monotonically as the hydration proceeds, and parts of the capillary pore space become isolated (Bentz et al., 1991).

2.5.5 **Model Execution Programs**

There are five main programs used for going from a two-dimensional image to a simulation of three-dimensional microstructure development. The first four programs are used as primary steps for executing the main hydration program. These programs are tabulated as follows:
Table (2.1): Steps in Execution of Three-Dimensional Cement Microstructure Model (Bentz 1997).

<table>
<thead>
<tr>
<th>Step</th>
<th>Program code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acquire and process two-dimensional image</td>
<td>statsimp.c</td>
</tr>
<tr>
<td>Determine autocorrelation for</td>
<td></td>
</tr>
<tr>
<td>$C_3S_a + C_2S$</td>
<td>corrcalc.c</td>
</tr>
<tr>
<td>$C_6S$</td>
<td>corrxy2r.c</td>
</tr>
<tr>
<td>$C_4A$ or $C_4AF$</td>
<td></td>
</tr>
<tr>
<td>Generate 3D particle image</td>
<td>genpartnew.c</td>
</tr>
<tr>
<td>Distribute phases in 3D image for silicates / aluminates</td>
<td>rand3d.f or rand3d.c</td>
</tr>
<tr>
<td>$C_3S/C_2S$</td>
<td>stat3d.c</td>
</tr>
<tr>
<td>$C_4A/C_4AF$</td>
<td>sinter3d.c</td>
</tr>
<tr>
<td>Execute hydration model</td>
<td>disrealnew.c</td>
</tr>
</tbody>
</table>

2.5.5.1 Two Dimensional Image of Cement Particles

There are some program codes such as statsimp.c, corrcalc.c and corrxy2r.c that are used to create 2D SEM images for the cement component. The analysis is based on the determination of the particle size distribution, phase volume fractions, phase surface area fraction and autocorrelation functions. The statsimp.c program determines 2D images for the cement structure showing every component in the cement phase using Bogue equations. The area percentage of the phases, the percentage of the phases comprising the particle surface can be determined for these images. Corrcalc.c and corrxy2r.c programs are used to measure the autocorrelation functions for the individual phases and certain combinations of phases in 2D dimension (Bentz, 1997).

2.5.5.2 Two-Dimensional to Three-Dimensional Conversion

There is a program called Genpartnew.c that is used for converting the cement phase particles into a 3D computational volume. The particle size distribution and the numbers of spherical particles of each phase of cement, calcium sulfate and mineral admixtures, and
calcium sulfate proportion to cement are used as input. The program allows the creation of any desired number of clusters by randomly moving each particle centroid in one-pixel increments and aggregating any particles in contact with one another during this process. The program allows the addition of a single flat plate aggregate to the 3D microstructure for studying the development of the interfacial transition zone microstructure. It also allows the employment of a burning algorithm to determine the percolation characteristics for the solid and pore phases. The number of pixels of porosity, cement, the three forms of calcium sulfate, pozzolans, inert filler, fly ash and aggregate are obtained as output (Bentz, 1997).

2.5.5.3 Filtering of Random Noise Particle Image

The rand3d.f or rand3d.c program coded in FORTRAN or C language is used to introduce the correct phase volume fraction and the correlation structure measured on the SEM image into the 3D cement particle image. A typical sequence is to separate the cement into silicates and aluminates, separate the silicates into C₃S and C₂S, and separate the aluminates into C₃A and C₄AF. A modification in the correlation function to convert it from 2D to 3D is obtained using programs stat3d.c and sintert3d.c using the hydraulic radius of each phase (Rh) as input in these programs.

A three-dimensional central image from the final 3D microstructure for cement 133 for w/c=0.30 as the conversion the image from 2D to 3D using programs Genpartnew.c and rand3d.c is shown in Figure (2.9).
Figure (2.9): Three-Dimensional Central Image from the Final 3D Microstructure for Cement 133 for w/c=0.30. Colour Assignments are Black- Porosity, Red- C$_3$S, Aqua- C$_2$S, Green- C$_3$A, Yellow- C$_4$AF, and Grey- Gypsum (Bentz 1997).

2.5.5.4 The Hydration Model

This model simulates the hydration process in 3D to determine the heat of hydration, chemical hydration and several coefficients in agreement with the experimental data generated for actual cements. A series of cellular automata-like rules are used for simulating the chemical reactions of the different phases. Cement model hydration reactions are shown as follows. The numbers written under every reaction expresses the molecular volume ratio between the different components of the reaction.

Silicate reactions:

\[
\begin{align*}
\text{C}_3\text{S} + 5.3 \text{ H} & \rightarrow \text{C}_{17}\text{SH}_4 + 1.3 \text{ CH} & \text{Eq. 2.20} \\
1 & 1.34 & 1.521 & 0.61
\end{align*}
\]

\[
\begin{align*}
\text{C}_2\text{S} + 4.3 \text{ H} & \rightarrow \text{C}_{15}\text{SH}_4 + 0.3 \text{ CH} & \text{Eq. 2.21} \\
1 & 1.49 & 2.077 & 0.191
\end{align*}
\]
Aluminate and Ferrite reactions:

\[
\begin{align*}
C_3A + 6H & \rightarrow C_3AH_6 & \text{Eq. 2.22} \\
1 & \quad 1.21 & \quad 1.69 \\
C_3A + 3C\tilde{S}H_2 + 26H & \rightarrow C_6A\tilde{S}_3H_{32} & \text{Eq. 2.23} \\
0.4 & \quad 1 & \quad 2.1 & \quad 3.2 \\
2C_3A + C_6A\tilde{S}_3H_{32} + 4H & \rightarrow 3C_4A\tilde{S}H_{12} & \text{Eq. 2.24} \\
0.2424 & \quad 1 & \quad 0.098 & \quad 1.278 \\
C_4AF + 3C\tilde{S}H_2 + 30H & \rightarrow C_6A\tilde{S}_3H_{32} + CH + FH_3 & \text{Eq. 2.25} \\
0.575 & \quad 1 & \quad 2.426 & \quad 3.3 & \quad 0.15 & \quad 0.31 \\
2C_4AF + C_6A\tilde{S}_3H_{32} + 12H & \rightarrow 3C_4A\tilde{S}H_{12} + 2CH + 2FH_3 & \text{Eq. 2.26} \\
0.348 & \quad 1 & \quad 0.294 & \quad 1.278 & \quad 0.09 & \quad 0.19 \\
C_4AF + 10H & \rightarrow C_4AH_6 + CH + FH_3 & \text{Eq. 2.27} \\
1 & \quad 1.41 & \quad 1.17 & \quad 0.26 & \quad 0.545 \\
\end{align*}
\]

The hydration process is executed in three stages: solution, diffusion and reaction. Each solid phase is characterized by two dissolution parameters, solubility flag which is equal to 1 for the soluble phases and a solution probability. The dissolution probability for C₃A and C₃S is about 0.8, while the dissolution probability for C₂S and C₄AF is about 0.2. The diffused particles due to the dissolution process react before a new dissolution step. Every hydration product may dissolve for another reaction as ettringite or may collide and nucleate as C-S-H. The state transition for 3D cement hydration model is illustrated in Figure (2.10).

2.5.5.5 The Hydration Model Enhancement

Since the appearance of the first version of the cement hydration model program CEMHYD3D by Bentz (1994), there are two new versions, Version 2.0 by Bentz (2000) and Version 3.0 by Bentz (2005). These improved the cement hydration model programs by producing a simulated hydration model more similar to the actual hydration process. The following section describes the hydration model enhancement.
Figure (2.10): The State Transition for 3D Cement Hydration Model (Bentz, 1995)

Version 2.0

- Induction period modelling

It is possible to simulate the induction period which is controlled by the nucleation and growth of the C-S-H phase. This period can be simulated in the CEMHYD3D model by proportioning the dissolution probabilities of the cement clinker phases to the square of the amount of formed C-S-H.

- Variable forms of calcium sulfate

In Version 1.0 of the cement hydration model, it is considered that there is only one form of calcium sulfate (gypsum). The reaction between the two other forms of calcium sulfate (hemihydrate and anhydrite) and the cement clinker phases is included in Version 2.0 to increase the utility of the computer codes.

- Temperature-variable C-S-H stoichiometry

The effect of the hydration temperature on the density of the C-S-H gel is simulated in Version 2.0 of CEMHYD3D. Equations 2.28 and 2.29 describe the relationships between
the molar volume of C-S-H \((\text{molarv})\) and temperature \((T)\) and between the water content in C-S-H structure \((\text{watercon})\) and temperature.

\[
\text{molarv}[C-S-H] = 1000 \times \left(108 - 8 \times \frac{T - 20}{80 - 20}\right) \text{mm}^3 / \text{mol} \quad \text{Eq. 2.28}
\]

\[
\text{watercon}[C-S-H] = 4.0 - 1.3 \times \frac{T - 20}{80 - 20} \quad \text{Eq. 2.29}
\]

- Variable temperature curing

Version 2.0 of CEMHYD3D includes the curing temperature of the cement paste after the hydration process such as that employed in steam curing by storing the desired curing temperature profile as an input file in the hydration program.

- Enhanced pozzolanic reactions

More accurate modelling of the reactions between silica (from silica fume or fly ash) and the cement hydration product CH to produce pozzolanic C-S-H is included in Version 2.0 of CEMHYD3D. The pozzolanic reaction is described in the following Equations:

\[
1.1 \text{CH} + 2.8 \text{S} + 2.8 \text{H} \rightarrow C_{13}S_{1.9} \quad \text{Eq. 2.30}
\]

\[
C_{13}S_{1.9} + 0.5 \text{H} \rightarrow C_{13}S_{1.9} + 0.6 \text{CH} \quad \text{Eq. 2.31}
\]

Version 3.0

- Individual phase reactivities

For simulating the individual reactivity of each of the clinker phases, a degree of hydration comparison between experimental and model results is executed. It is found that the dissolution probabilities of the \(C_2S\) and \(C_4AF\) in the model should reduce by 50% to give results that agree with the experimental result.

- Influence of non-reactive fine fillers
This version includes the existence and reaction of some fine fillers in the cement composition such as rutile (TiO₂) of 0.5 µm average particle size. It was modelled in the CEMHYD3D simulation by 1 voxel (1 µm) particles of inert material.

- Pore solution composition and its influence on hydration

Only the formation of solid hydration products without any information about the composition of the pore solution filling the pores during the hydration is considered in the previous versions. In Version 3.0 of CEMHYD3D, a new program pHpred.c has been added to the CEMHYD3D codes to predict the pore solution composition and its electrical conductivity during the hydration. This program also considers the dissolution of sodium and potassium (sulfates) to supply ions in the pore solution and to supply ions absorbed in the conventional and pozzolanic C-S-H structure.

- Incorporation of reactions for limestone in CEMHYD3D

The chemical reaction between calcium carbonate (limestone) filler and cement has been included in Version 3.0 of CEMHYD3D. This reaction is described in the following Equation.

\[
3(\text{CaO})_3(\text{Al}_2\text{O}_3).\text{CaSO}_4.12\text{H}_2\text{O} + 2\text{CaCO}_3 + 18\text{H}_2\text{O} \rightarrow 2(\text{CaO})_3(\text{Al}_2\text{O}_3).\text{CaCO}_3.11\text{H}_2\text{O} \\
+ (\text{CaO})_3(\text{Al}_2\text{O}_3).3\text{CaCO}_3.32\text{H}_2\text{O}
\]

Eq. 2.32

- Preliminary incorporation of reactions for slag in CEMHYD3D

The reaction of the slag with calcium hydroxide produces a mixture of a C-S-H type gel with lower Ca/Si ratio than the conventional C-S-H. This C-S-H type can be simulated by supplying its specific gravity, molar volume and Ca/Si and H₂O/Si molar ratios as a data file outlined in the execution of the 3D cement hydration model.
2.6 Summary

This chapter includes a review of the cement hydration mechanism, the use of glass powder in concrete, and cement hydration modelling. To the knowledge of the author, it is noticed from the literature that the chemical behaviour of glass powder concrete has not been studied. The existing computer models that simulate the hydration of the cement did not account for the hydration of the cementitious materials, which are added to the cement. Only the CEMHYD3D model simulates the hydration of the cementitious materials such as fly ash, silica fume and slag inside the cement hydration matrix. The computer simulation of the glass powder blended cement hydration has not been addressed because of the lack of the chemical information of the glass powder blended cement hydration. Hence, the aim of this work is to study the chemical behaviour of the glass powder blended cement paste experimentally. The computer simulation of the glass powder blended cement hydration based on the experimental results will then be addressed.
CHAPTER 3

HYDRATION AND MICROSTRUCTURE OF ACTIVATED GLASS POWDER

3.1 Introduction

The use of recycled glass in the construction industry, particularly in the concrete industry, is relatively new. Nowadays, research investigations deal with the use of recycled glass as fine aggregate, course aggregate, fine filler and cement-replacement material depending on the degree of grinding of the glass. The main interest in this research is to study the behaviour of glass powder, with certain fineness, as a pozzolanic material. In order to establish specifications for the use of glass powder as a pozzolanic material in concrete, in the similar way to slag and fly ash, information about the pure glass powder hydration reaction, GP–CH hydration reaction and GP-blended cement hydration reaction is needed. In this chapter, experimentally-driven information on glass powder as a cementitious material is presented. Some models describing the hydration of the glass powder with and without CH are also developed in this chapter. Experimental testing is carried out to explain the behaviour of glass powder hydration.

Models established in this chapter are validated using the results of the experiments that are carried out on the activated glass powder. The results obtained in this chapter are also used
in Chapter 4 of this thesis, in which reaction models for glass powder-blended cement are developed.

### 3.2 Glass Powder Composition

In order to quantify the hydration reaction and determine the composition of the main hydration product C-S-H, the composition and the chemical formula of the glass powder have to be investigated. There are two main assumptions for the glass powder which are:

1. The glass powder grains constitute a homogeneous mixture of all its oxides.
2. All oxides in the glass powder react congruently to give the hydration products.

The glass powder oxide compositions are shown in Table 3.1 as a mass percentage.

#### Table (3.1): The Glass Powder Oxide Compositions

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>TiO₂</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
<th>PF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(S)</td>
<td>(A)</td>
<td>(F)</td>
<td>(C)</td>
<td>(M)</td>
<td>(T)</td>
<td>(K)</td>
<td>(N)</td>
<td>(S)</td>
<td>(P)</td>
</tr>
<tr>
<td>Mass percentage</td>
<td>69.4</td>
<td>1.7</td>
<td>0.5</td>
<td>10.6</td>
<td>1</td>
<td>0.1</td>
<td>0.6</td>
<td>12.8</td>
<td>&gt;0.1</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Two different simple chemical formulas are proposed to describe the models.

1. The first formula considers the oxides to constitute more than 99% of the glass powder mass. This formula is written as \( C_{n_{SiO2}} S_{n_{Al2O3}} N_{n_{Fe2O3}} A_{n_{CaO}} M_{n_{MgO}} T_{n_{TiO2}} K_{n_{K2O}} N_{n_{Na2O}} S_{n_{SO3}} \).

2. The second formula considers that the oxides constitute more than 90% of the glass powder mass and neglect the other 10% of its weight which contains the minor oxides. This formula is written as \( C_{n_{SiO2}} S_{n_{Al2O3}} N_{n_{Fe2O3}} A_{n_{CaO}} M_{n_{MgO}} T_{n_{TiO2}} K_{n_{K2O}} N_{n_{Na2O}} \).

The moles of oxides of the glass powder can be calculated using the equation, Eq. 3.1 as follows:
in which \( n_i^G \) is the number of moles in oxide \( i \) in the glass powder, \( m^G \) is the mass of the glass powder and \( M_i \) is the molar mass of the oxide \( i \).

The molar mass of the glass powder can be calculated using Eq. 3.2 and Eq. 3.3 as follows:

\[
M^{GP} = \sum (y_i M_i) \tag{Eq. 3.2}
\]

\[
y_i = \frac{x_i^G / M_i}{\sum (x_i^G / M_i)} \tag{Eq. 3.3}
\]

where \( M^{GP} \) is the molar mass of the glass powder, \( y_i \) is the molar fraction of oxide \( i \) in the glass powder and \( x_i^G \) is the mass fraction of oxide \( i \) in the glass powder.

### 3.3 Glass Powder Hydration Models

Three different models are proposed to describe the hydration reaction of the pure glass powder and GP-CH as well.

#### 3.3.1 Model A

The following proposed model is a general chemical equation simulating the hydration of the pure glass powder using the first formula proposed for the glass powder. In this model, the glass powder reacts with water to produce two different hydration products. The first product is C-S-H with some substitution ions of Na and Al, the second product is hydrotalkite.

\[
C_{n_{C-S-H}}^{\nu_1}A_{\nu_2}^\theta M_{\nu_3}^{\theta} + n_{H_2}H \rightarrow n_{C-S-H} C_s S N_c A_h H_k + n_{H_2} M_s A H_{13} \tag{Eq. 3.4}
\]
where $n_c^G, n_s^G, n_a^G, n_m^G$ are the moles of oxides C, S, N, A, and M respectively, $n_H$ is the moles of water required for the reaction and $n_{C-S-H}$ and $n_{HT}$ are moles of the hydration products C-S-H and hydrotalcite.

By equilibrating Eq. 3.4, the $C/S$, $A/S$ and $N/S$ ratios can be calculated.

$$n_c^G = a \times n_{C-S-H}$$

$$n_s^G = n_{C-S-H}$$

$$n_a^G = n_{n_l}^G - n_{n_l}^G = c \times n_{C-S-H}$$

$$n_n^G = b \times n_{C-S-H} + n_{HT}$$

$$n_m^G = 5n_{HT}$$

$$n_H = g \times n_{C-S-H} + 13n_{HT}$$

where,

$$a = \frac{n_c^G}{n_s^G}, b = \frac{n_a^G - n_m^G}{n_s^G}, c = \frac{n_n^G - n_{n_l}^G}{n_s^G}$$

and

$$a=C/S, b=A/S, c=N/S$$

where, $n_{n_l}^G$ is the moles of alkalis in the pore solution.

There are three different special cases for the reaction products of the hydration equation.

Case 1: No Al substitution and no Na in the C-S-H structure:

Here, we assume that the produced C-S-H is pure without any substitution of $Al$ or $Na$. This means that the entire $Al$ will contribute in the hydrotalcite structure and the entire $Na$ will contribute in the pore solution.

Hence, substituting $b = 0$ in Eq. 3.6, we obtain:
and substituting \( c = 0 \) in Eq. 3.6, we obtain:

\[
n_{ps}^G = n_n^G
\]  
Eq. 3.9

Case 2: All the alkali ions remain in the pore solution and the Al ions contribute to both the C-S-H and hydrotalkite structures.

Case 3: Neglecting the existence of Mg, all the Al ions contribute to the C-S-H structure and the alkali ions contribute to both C-S-H structure and pore solution.

\[
n_{ps}^G = bn_{C-S-H}
\]  
Eq. 3.10

and

\[
a = \frac{n_c^G}{n_n^G}, \quad b = \frac{n_a^G}{n_n^G}, \quad c = \frac{n_n^G - n_{ps}}{n_n^G}
\]  
Eq. 3.11

### 3.3.2 Model B

This is another model that describes the hydration of pure glass powder using the second proposed formula for the glass powder composition.

\[
C_{n_c^G}S_{n_s^G}N_{n_m^G} + n_HH \rightarrow n_{C-S-H}C_aSN_cH_g
\]  
Eq. 3.12
3.3.2.1 Model Assumptions

In the glass powder chemical formula, the major oxides (≥90% of the total mass) in the glass powder composition are considered and the minor oxides (<10% of the total mass) are neglected.

For the hydration equation, the main and only hydration product is GP C-S-H.

The equilibrium equation gives:

\[ n_c^G = a \times n_{C-S-H} \]
\[ n_s^G = n_{C-S-H} \]
\[ n_n^G = n_n^G - n_{ps} = c \times n_{C-S-H} \]
\[ n_H = g \times n_{C-S-H} \]

Eq. 3.12

3.3.3 Model C

\[ C_{n_e} S_{n_i} N_{n_a}^G + n_{ch} CH + n_H H \rightarrow n_{C-S-H} C_a S N_e H g \]  

Eq. 3.13

This model is proposed to simulate the hydration of the GP-CH reaction using the assumptions of model (B). In this equation, the glass powder will react with the calcium hydroxide in contact with water to produce GP C-S-H. In the model, \( n_{ch} \) is the consumed moles of the CH during the glass powder hydration. The equation equilibrium of this model can be expressed as follows:

\[ n_c^G + n_{ch} = a \times n_{C-S-H} \]
\[ n_s^G = n_{C-S-H} \]
\[ n_n^G = n_n^G - n_{ps} = c \times n_{C-S-H} \]
\[ n_H + n_{ch} = g \times n_{C-S-H} \]

Eq. 3.14

where,
3.4 Experimental Program

3.4.1 Introduction

The main objective of this experimental work is to examine the reactivity of the GP with the CH in an activated medium. To accept the GP as a pozzolanic material to be used in concrete, it is necessary to have complete chemical and physical behaviour and characteristics of the GP reaction inside the cement hydration matrix. The reaction between the GP and CH in different activated media is a preliminary step to make sure that the GP has a pozzolanic nature and can positively affect the cement hydration process.

Another main objective of this work is to create a chemical formula simulating the hydration reaction between the GP and CH. The obtained information will be used in the computer simulation of the GP-blended cement hydration.

Five different tests were carried out to evaluate the hydration behaviour of the GP and CH. These tests are:

3. Non-evaporable water content test,
4. pH test,
5. determination of reacted quantity of the GP,
6. pore solution alkalinity due the Na release during the hydration and
7. X-R-D tests investigating the CH consumption with time.

In addition, SEM images were taken to track the microstructure changes with time.

The following sections describe the details of the experimental program including the used materials, used parameters studied, preparation of specimens, methodology, and analysis of the results. The implementation of the proposed chemical formula for the GP and CH
hydration of GP using these results is also discussed. Finally conclusions of the experimental work are drawn.

3.4.2 Materials

3.4.2.1 Glass Powder

Recycled glass is used in this investigation. This glass was cleaned and ground to a homogeneous powder, then, sieved to obtain a glass powder GP of maximum particle size of 100 µm using and BET specific surface area of 1.72m²/g. Figure (3.1) represents the particle size distribution of the glass powder according to ASTM C430-9C430-96. It shows that the powder matrix is a mix of micro and sub-micro particles. It consists of about 5% sub-micro particles and about 95% micro-particles.

![Particle size distribution](image)

**Figure (3.1): Particle Size Distribution of the Used Glass Powder**

Figure (3.2) represents the microstructure image of the glass powder. The figure shows that every big particle is surrounded by small particles. The bigger particles attract the fine particles to set through its voids and on its surface.
X-R-D analysis was done to check the crystalline nature of the glass powder. Figure (3.3) shows that GP is an amorphous material and that there are no noticeable peaks representing any of its compounds.

Figure (3.2): The Microstructure Image of the Glass Powder

Figure (3.3): XRD Analysis of the Used Glass Powder
3.4.2.2 Calcium Hydroxide

The calcium hydroxide CH used has a nominal size of 97% minimum passing a 325 mesh. Table (3.2) represents the CH composition as weight percentage.

**TABLE (3.2): CH COMPOSITION AS WEIGHT PERCENTAGE**

<table>
<thead>
<tr>
<th>Chemical Analysis</th>
<th>Percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
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<tr>
<td>Ca(OH)$_2$</td>
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</tr>
<tr>
<td>CaCO$_3$</td>
<td>1.70</td>
</tr>
<tr>
<td>MgO</td>
<td>1.10</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.10</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
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</tr>
<tr>
<td>Fe$_2$O$_3$</td>
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</tr>
<tr>
<td>S</td>
<td>0.028</td>
</tr>
<tr>
<td>LOI</td>
<td>23.00</td>
</tr>
<tr>
<td>Available CaO</td>
<td>71.50</td>
</tr>
</tbody>
</table>

3.4.3 Parameters Studied

In this part of the research work, which focuses on the hydration and microstructure of activated glass powder, a total of 105 paste specimens were cast and categorized into 3 main groups. The quantity of the added GP was kept constant for all the test specimens. CH content was added as a ratio of the GP content. The different CH/GP ratios studied (by weight) were 0, 0.5, 10, 20, 30, 40, 60, and 100%. The chosen CH ratios were varied to examine the GP reactivity at low and high amounts of CH. The activation temperature was another parameter. Three different temperatures were chosen; these are 25, 40, 80°C to activate the hydration reaction of the GP and CH. The water solid ratio w/s was 0.5 for all cast specimens. Specimens were tested at 0, 1, 3, 7, and 14 days of hydration. Table (3.3) represent the different parameters studied in this experimental investigation.
Table (3.3): The Parameters of the Experimental Investigation

<table>
<thead>
<tr>
<th>Groups</th>
<th>GP Addition Ratio (%)</th>
<th>CH Addition Ratio (%)</th>
<th>((\text{CH}/\text{GP})) Ratio (%)</th>
<th>w/s Ratio</th>
<th>Activation Temperature</th>
<th>Testing Time (Days)</th>
</tr>
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<td>0</td>
<td>0.5</td>
<td>25 °C</td>
<td>7</td>
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<td>0.5</td>
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<td>50</td>
<td>100</td>
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<tr>
<td>III</td>
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<td>0</td>
<td>0</td>
<td>0.5</td>
<td>80 °C</td>
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<td>0.5</td>
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<td>100</td>
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3.4.4 Preparation of Test Specimens

The different groups were cast at room temperature 25°C. The solid materials and water were mixed together using a food mixer for three minutes to make sure that all the materials are mixed well. The specimens were cast in 15ml secured plastic tubes to make sure that no water evaporation can occur during the hydration. Then, each group was put at its constant activated temperature for the specified time of testing.

The preparation of the specimens for testing was completed in four different steps. The specimens were first released from the cast tubes for grinding. Then, the specimens were dried for 24 hours at 110°C in an oven to evaporate all the free water to simply prevent any
further hydration. The specimens were then ground again and sieved to obtain a powder of maximum particle size of 100µm. Afterwards, the specimens were stored in secured tubes until testing.

3.4.5 Tests

Five different tests were carried out to test the powder specimens to determine the chemical and physical characteristics of the GP-CH hydration reaction. Descriptions of these tests are outlined in the following sections.

3.4.5.1 Determination of Degree of Hydration Using Non-Evaporable Water Content

According to the test carried out by Neithalath et al. (2007), the combined water in the different specimens can be determined. This test determines the water consumed during the GP-CH hydration. A powder amount of weight of (2) gm was placed in a 1010 °C oven to release all the compound water. The specimen was then weighed to determine the weight loss due to water evaporation. The non-evaporable water content ($w_n$) is calculated using Eq. 3.15 as follows:

$$w_n = \frac{w_i - w_f}{w_s}$$  \hspace{1cm} \text{Eq. 3.15}

in which $w_i$ is the weight of the specimen before being put in the oven and $w_f$ is the specimen weight after losing the compound water.

3.4.5.2 pH

The pH test was carried out according to ASTM D1293-99(2005) for the powder specimens using a "HACH ONE pH METER" at Soil Mechanics Laboratory, Civil Engineering Department, University of Sherbrooke, as shown in Figure (3.4), to determine the alkalinity
of the specimens at different times before, during and after the hydration. The hydration degree of the GP is affected by the pH value of the activator. The pH measurement indicates the alkalinity of the pore solution of the hydrated system.

![Image of pH measurement apparatus](image)

**Figure (3.4): The Used Apparatus of pH Measurement**

### 3.4.5.3 Un-reacted GP

This test is used to determine the residual amount of GP that never reacted during the hydration. By subtracting this amount from the total addition of the GP, the total amount of GP consumed during the hydration can be calculated. This information helps in proposing the chemical formula of the GP-CH reaction.

Two grams of the powder specimen was mixed with 50ml of distilled water and 20ml of nitric acid. The mixture was then boiled for 10 minutes to make sure that all the basic compounds in solution, such as CH and C-S-H, are decomposed due to the presence of the
nitric acid as a decomposer. The remaining solids in the solution after that constitute the un-reacted GP. This un-reacted GP can be collected on a filter paper by filtering the solution. By knowing the weight of the filter paper before the test ($w_f$) and the weight of the filter paper and GP after being dried for 24 hours at 110 °C in a drying oven, ($w_{f+GP}$), the weight of un-reacted $GP$ can be calculated using Eq. 3.16 as follows.

$$w_{unr-GP} = w_{f+GP} - w_f$$

Eq. 3.16

3.4.5.4 Na Concentration

After mixing the water with the assigned portions of GP and CH, the resulting liquid phase is referred to as the “pore solution”, which contains a substantial amount of ions. At this stage, there is a possibility that when all the alkali ions are released in the pore solution from the reactants, the hydration process will be activated. Due to the presence of the Na ions in the GP composition with high proportion, the presence of these ions in the pore solution may increase the reactivity of the reactants. This is attributed to the increase of the alkalinity level of the pore solution which may also affect the microstructure of the hydration products.

One gram of the specimen powder was mixed with 100ml of distilled water, and then the mixture was boiled for ½ hour to make sure that all the alkali ions are released from powder and dissolved in the solution. The solution was filtered in 300ml distilled water to obtain a clear solution without solids.

According to the specification ASTM-C441 (2005), the “PERKIN ELMER-AAnalyst 300” flame photometry apparatus at Environmental Laboratory was used, Civil Engineering Department, University of Sherbrooke, as shown in Figure (3.5), to measure the Na concentration in the pore solution.
3.4.5.5 X-Ray Diffraction (XRD) Analysis

XRD analysis is used in this work as an approximate way to calculate the amount of CH crystals in the powder. Due to the crystalline nature of the CH, the presence of CH in any compound can be investigated using XRD analysis. The CH crystals have a known peak positions at 2θ=18, 28 and 34°. The amount of CH in any compound can be determined approximately by comparing the CH peak intensities between the known and unknown amounts of CH compounds.

By knowing the amount of un-reacted CH, the consumed CH during the hydration reaction with the GP can be easily determined. This actually facilitates proposing the chemical formula of the GP-CH hydration reaction.
3.4.6 Analysis of Results

3.4.6.1 Introduction

The following sections present the chemical and physical behaviour of the glass powder during its hydration with and without CH. The following experimental results represent the reactivity of the GP in terms of the degree of hydration, pH, and Na concentration in the pore solution due to the reaction. Then, X-R-D test results were analyzed focusing on the reaction behaviour in certain zone of the CH peaks to determine the CH consumption due to the hydration. Finally, SEM images of the GP-CH specimens before and after the hydration were presented to indicate the microstructure changes due to the hydration.

3.4.6.2 Degree of Hydration

The degree of hydration of the glass powder is calculated from Eq. 3.17 as follows:

\[ D.O.H = \frac{(w_n)}{(w_n)_{max}} \]  

Eq. 3.17

where:

- \( D.O.H \) is the degree of hydration of any specimen at a certain testing time and certain activation temperature,
- \( (w_n) \) is the non-evaporable water content of any specimen at a certain testing time and certain activation temperature, and
- \( (w_n)_{max} \) is the maximum non-evaporable water content for the specimen.

In this work, the \( (w_n)_{max} \) is obtained for all the specimens groups after 14 days of hydration at 80 °C. Figures (3.6 to 3.13) show the relationships between the \( D.O.H \) and time for each CH/GP ratio at different activation temperatures, 25, 40 and 80°C. As shown in all the figures, the degree of hydration increases with time and with increasing activation temperature. For the 0 and 0.5 CH/GP ratios, there are large differences in the degree of hydration with time due to the increase of the activation temperature. At temperature of
25°C, the degree of hydration is very low and increases slowly with time up to 14 days of hydration. However, at higher temperatures (40 and 80°C) the degree of hydration increases to its maximum value at 7 days of hydration. For the 10, 20 and 30% CH/GP ratio specimens, the degree of hydration differences due to the changing of the activation temperature decreases. By increasing the CH/GP ratio after that, the differences in the degree of hydration values due to the changing of the activation temperature are slight different and the maximum degree of hydration is obtained after 3 days of hydration.

From the different curves, as the time and the activation temperature affect the degree of hydration, the degree of hydration also increases by increasing the CH/GP ratio. For high CH/GP ratio specimens, the degree of hydration attains its maximum value earlier than the specimens of low CH/GP ratio. The figures also show that there is an optimum CH/GP addition to obtain the maximum degree of hydration; this ratio is CH/GP = 20%. The effect of increasing the CH dose on the degree of hydration decreases for the specimens of CH/GP ratio more than 20%.

![Figure (3.6): Relationships between D.O.H. and Time for (CH/GP) % = 0% at Different Activation Temperatures, 25, 40 and 80°C](image)

57
Figure (3.7): Relationships between D.O.H. and Time for (CH/GP) % = 0.5% at Different Activation Temperatures, 25, 40 and 80°C

Figure (3.8): Relationships between D.O.H. and Time for (CH/GP) % = 10% at Different Activation Temperatures, 25, 40 and 80°C
Figure (3.9): Relationships between D.O.H. and Time for (CH/GP) % = 20% at Different Activation Temperatures, 25, 40 and 80°C

Figure (3.10): Relationships between D.O.H. and Time for (CH/GP) % = 30% at Different Activation Temperatures, 25, 40 and 80°C
Figure (3.11): Relationships between D.O.H. and Time for (CH/GP) % = 40% at Different Activation Temperatures, 25, 40 and 80°C

Figure (3.12): Relationships between D.O.H. and Time for (CH/GP) % = 60% at Different Activation Temperatures, 25, 40 and 80°C
3.4.6.3 pH

pH gives an indication of the GP reactivity. For all glassy composition materials, there is no reactivity if the pH < 9, (Poul 1977). The reactivity increases by increasing the pH over 9.

Figures (3.14 to 3.16) show the relationship between the pH values and the CH/GP ratio at different testing times and different activation temperatures. The figures show that the main increase of the pH values is obtained for the specimens having CH/GP ratios from 0 to 20%. By increasing the CH/GP ratio above 20%, the pH values are almost constant. This means that the maximum reactivity of the GP can be obtained for the specimens of CH/GP ratio = 20%. After this ratio, there is no noticeable increase in the glass reactivity.

Figures (3.17 to 3.19) show that the pH values for all the specimens increases with the time until the first day of hydration. Then, it slightly decreases with time up to 14 days of hydration. This is due to the release of the Na ions from the GP structure during the hydration which increases the pH values. Afterwards, the formation of the hydration product (GP C-S-H) can absorb part of the released Na ions which cause a decrease in the
pH values with time. There is no a significant effect of increasing the hydration temperature on increasing the pH. For the 0 and 0.5% CH/GP ratios, there are noticeable differences of the pH values with time. By increasing the CH/GP ratio, these differences decrease with time.

To indicate the relationship between the degree of hydration and the pH, Figure (3.20) shows that the degree of hydration increases by increasing the pH values. For the specimens of 0 and 0.5% CH/GP ratio, the hydration reaction of the glass powder starts at pH > 9.5, then the reactivity of the glass powder increases by increasing the pH of the solution. There is a linear increase of the degree of hydration by increasing the pH until pH= 10.5. After this value, the degree of hydration increases at a higher rate by increasing the pH. For the CH/GP ratio of 10 to 100%, the degree of hydration increases rapidly when the pH reaches to values exceed 10.5. This means that the best performance of the GP reactivity can be obtained in the range 10.5<pH<11.5 depending on the CH/GP ratio.

![Figure (3.14): Relationships between pH and CH/GP Ratio at Different Ages at Activation Temperature, 25°C](image)

Figure (3.14): Relationships between pH and CH/GP Ratio at Different Ages at Activation Temperature, 25°C
Figure (3.15): Relationships between pH and CH/GP Ratio at Different Ages at Activation Temperature, 40°C

Figure (3.16): Relationships between pH and CH/GP Ratio at Different Ages at Activation Temperature, 80°C
Figure (3.17): Relationships between pH and Time for Different CH/GP Ratios at Activation Temperature, 25°C

Figure (3.18): Relationships between pH and Time for Different CH/GP Ratios at Activation Temperature, 40°C
Figure (3.19): Relationships between pH and Time for Different CH/GP Ratios at Activation Temperature, 80 °C

Figure (3.20): Relationships between D.O.H. and pH for Different CH/GP Ratios at Activation Temperature, 80 °C
3.4.6.4 Reacted GP

Many factors affect the reactivity of any glass composition material such as slag and glass powder. These factors are its oxides composition, pH, particle size distribution, and....etc. The particle size distribution and maximum particle size are important factors affecting the glass material reactivity. As the particles are small, the reactivity increases because the internal bond between the small particles can be broken more easily due to the reaction than the big particles. Also the specific area which is in contact with water increases in the small particles than that in the bigger particles. As shown in Figure (3.1), the maximum particle size of the glass powder used is 100µm, d_{50}=6µm and d_{90}=23µm. Hence, if 50% of the glass powder reacts, this means that all the particles of size smaller than or equal to 6µm participate in the reaction.

![Figure (3.21): Relationships between GP(R) Ratio and CH/GP Ratio at Different Ages at Activation Temperature, 25 °C](image-url)
Figure (3.22): Relationships between GP(R) Ratio and CH/GP Ratio at Different Ages at Activation Temperature, 40 °C

Figure (3.23): Relationships between GP(R) Ratio and CH/GP Ratio at Different Ages at Activation Temperature, 80 °C
Figures (3.21 to 3.23) show the relationship between the reacted GP and CH/GP ratio developed with time at different activation temperatures. As shown in the figures, the amount of reacted GP increases by increasing the CH/GP ratio until 20%. By increasing the CH/GP ratio over 20%, there is no more consumption of the GP. This means that there is an optimum consumption of the GP with the CH, which depends on the GP particles sizes. For the specimens which are hydrated at temperature 80°C after 14 days, about 25% of the total weight of GP used had reacted for a maximum reactive particle size of 2.5µm.

3.4.6.5 Alkalis in Pore Solution

The glass powder contains about 13% of alkalis material, most of this is sodium oxide. The alkalis are supposed to leave the glass structure during the hydration to stay in the pore solution or enter the hydration products structure due to breaking the internal bond of the glass structure during the hydration reactions.

Figures (3.24 to 3.26) show the relationship between the CH/GP ratio and the (Na/GP)% ratio, which is the ratio between the weight of the released Na over the weight of the GP, with time for the different hydrated specimens at temperatures 25, 40 and 80°C. The figures show that the Na concentration in the pore solution increases with time and with increasing the CH/GP ratio in the specimens. According to the trend of the curves, the released Na in the pore solution increases by increasing the CH/GP ratio until CH/GP =20%; then it decreases to be constant for the higher CH/GP ratio specimens. This is because there are continuous reactions between the GP and CH until CH/GP =20%, during the reaction period, the Na is released from the GP structure to stay in the pore solution.

3.4.6.6 XRD Analysis

In the current work, the XRD analysis is carried out in the range from 2θ=16° to 2θ=36°. This zone is chosen to cover the CH peak zones which are at 2θ=18, 28 and 34° in order to monitor the CH consumption with time.
Figure (3.24): Relationship between CH/GP Ratio and Na/GP Ratio with Time at Activation Temperatures 25°C

Figure (3.25): Relationship between CH/GP Ratio and Na/GP Ratio with Time at Activation Temperatures 40°C
Figure (3.26): Relationship between CH/GP Ratio and Na/GP Ratio with Time at Activation Temperatures 80 °C

Figures (3.27 to 3.29) show the 2θ-intensity relationships for all the specimens at 14 days of hydration at different activation temperatures of 25, 40 and 80°C. For all the figures, the 0 and 0.5% CH/GP ratio curves show that there are no CH peaks and pure glass amorphous noises occur along the studied zone. The CH peaks start to appear in specimen of CH/GP RATIO OF 30% at 2θ=18°, 28° and 34° and the peak intensities increase by increasing the amount of the CH in the tested compound. By increasing the CH/GP ratio, the amorphous nature of the specimen structure decreases, which appears as a decrease in the amorphous noise intensity of the 2θ-intensity curves.

Figure (3.30) shows the hydration development with time for the specimens of CH/GP ratio=20% hydrated at a temperature of 80°C. As shown in this figure, the intensities of the CH peaks decrease with time to disappear completely after 14 days of hydration. This means that all the amount of CH in the specimens of CH/GP ratio=20% are totally consumed after 14 days of hydration at 80°C. But for specimens of CH/GP ratio > 20% in the same conditions, there are some amounts of CH remaining in the compound that do not react with the GP.
Figure (3.27): 2θ-Intensity Relationship for All CH/GP Ratios at 14 days of Hydration at Activation Temperature, 25°C
Figure (3.28): 20-Intensity Relationship for All CH/GP Ratios at 14 days of Hydration at Activation Temperature, 40 °C
Figure (3.29): 2θ-Intensity Relationship for All CH/GP Ratios at 14 days of Hydration at Activation Temperature, 80°C
3.4.6.7 CH Consumption

There is no direct way to determine the amount of consumed CH during the hydration process. Hence, X-R-D analysis is used to indirectly calculate the CH consumption. The method that can be used to determine the amount of any crystalline material using the X-R-D analysis was first developed at University of Sherbrooke (Fares and Tagnit-Hamou, 2007). First, different samples of CH/(GP+CH) ratios of 0, 4, 8, 16, 100% are prepared. Then all the samples were examined by XRD diffraction at a range of 2θ from 16 to 36, where θ is the diffraction angle. The values of the maximum peak intensities of the CH are then determined. Figure (3.31) shows the relationship between the CH/(GP+CH) ratios of the prepared samples and the values of the maximum peak intensities of the CH. It is found that there is a linear relationship between the CH/(GP+CH) ratios as a function of the maximum peak intensities of the CH. Equation (3.18) represents the linear relationship between the CH/(GP+CH) ratios as a function of the maximum peak intensities of CH. This relationship can be best fitted as:
\[ y = 12.988x + 51.549 \quad \text{Eq. 3.18} \]

where, \( y \) is the CH maximum peak intensity and \( x \) is CH/(GP+CH) ratio of the different samples. This equation can be used to determine the CH/(GP+CH) ratio for any sample by knowing its CH maximum peak intensity using the XRD analysis. Table (3.4) represents the CH consumption of all the hydrated specimens at different hydration temperatures and times. As it is shown in table (3.4) the maximum consumption of the CH due the GP hydration with time and with an increase in the activation temperature is obtained in the specimen of CH/GP ratio equal 20%.

![Graph showing the relationship between CH/(GP+CH) ratios and the values of the maximum peak intensities of the CH.](image)

**Figure (3.31):** Relationship between CH/(GP+CH) Ratios of the Prepared Samples and the Values of the Maximum Peak Intensities of the CH.

Figures (3.32 to 3.34) show the relationship between the CH consumption rates, which is the ratio between the amount of CH consumed after time \( t \) of hydration over the total amount of CH before the hydration, developed with time for the different tested groups. All the amount of CH added for the specimens of the CH/GP ratio of 10%, hydrated at 25°C, are consumed during the first 7 days of hydration. For the hydrated specimens at 40 and 80°C, the entire CH amount is consumed immediately at the beginning of the hydration. For the specimens of CH/GP ratio of 20% and hydrated at 25°C, about 90% of the total CH
amount are consumed during the hydration period of 14 days. However, the CH amount is entirely consumed during the same hydration period for the same specimens hydrated at 40 and 80°C. For the other specimens of CH/GP ratio greater than 20%, not all the CH amount is consumed during the hydration period of 14 days.

Table (3.4): The CH Consumption of the All Hydrated Specimens at Different Hydration Temperature and Time

<table>
<thead>
<tr>
<th>(CH/GP)</th>
<th>(CH/CH+GP)</th>
<th>(w/GP+CH)</th>
<th>Activation Temperature</th>
<th>Consumed CH/(GP+CH)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>%</td>
<td>Ratio</td>
<td>25°C</td>
<td>1 Day</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>25°C</td>
<td>-----</td>
</tr>
<tr>
<td>0.5</td>
<td>0.497</td>
<td>0.5</td>
<td>25°C</td>
<td>0.497</td>
</tr>
<tr>
<td>10</td>
<td>9.09</td>
<td>0.5</td>
<td>25°C</td>
<td>3.34</td>
</tr>
<tr>
<td>20</td>
<td>16.667</td>
<td>0.5</td>
<td>25°C</td>
<td>2.61</td>
</tr>
<tr>
<td>30</td>
<td>23.07</td>
<td>0.5</td>
<td>25°C</td>
<td>1.14</td>
</tr>
<tr>
<td>40</td>
<td>28.57</td>
<td>0.5</td>
<td>25°C</td>
<td>1.26</td>
</tr>
<tr>
<td>60</td>
<td>37.5</td>
<td>0.5</td>
<td>25°C</td>
<td>0.5</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>0.5</td>
<td>25°C</td>
<td>0.2</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>40°C</td>
<td>-----</td>
</tr>
<tr>
<td>0.5</td>
<td>0.497</td>
<td>0.5</td>
<td>40°C</td>
<td>0.497</td>
</tr>
<tr>
<td>10</td>
<td>9.09</td>
<td>0.5</td>
<td>40°C</td>
<td>8.85</td>
</tr>
<tr>
<td>20</td>
<td>16.667</td>
<td>0.5</td>
<td>40°C</td>
<td>6.33</td>
</tr>
<tr>
<td>30</td>
<td>23.07</td>
<td>0.5</td>
<td>40°C</td>
<td>5.65</td>
</tr>
<tr>
<td>40</td>
<td>28.57</td>
<td>0.5</td>
<td>40°C</td>
<td>5.42</td>
</tr>
<tr>
<td>60</td>
<td>37.5</td>
<td>0.5</td>
<td>40°C</td>
<td>1.31</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>0.5</td>
<td>40°C</td>
<td>0.568</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>80°C</td>
<td>-----</td>
</tr>
<tr>
<td>0.5</td>
<td>0.497</td>
<td>0.5</td>
<td>80°C</td>
<td>0.497</td>
</tr>
<tr>
<td>10</td>
<td>9.09</td>
<td>0.5</td>
<td>80°C</td>
<td>9.09</td>
</tr>
<tr>
<td>20</td>
<td>16.667</td>
<td>0.5</td>
<td>80°C</td>
<td>8.12</td>
</tr>
<tr>
<td>30</td>
<td>23.07</td>
<td>0.5</td>
<td>80°C</td>
<td>6.01</td>
</tr>
<tr>
<td>40</td>
<td>28.57</td>
<td>0.5</td>
<td>80°C</td>
<td>5.77</td>
</tr>
<tr>
<td>60</td>
<td>37.5</td>
<td>0.5</td>
<td>80°C</td>
<td>2.96</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>0.5</td>
<td>80°C</td>
<td>5.07</td>
</tr>
</tbody>
</table>
Figure (3.32): Relationship between CH Consumption Rate and Time for Different CH/GP Ratios at Activation Temperature, 25°C

Figure (3.33): Relationship between CH Consumption Rate and the Time for Different CH/GP Ratios at Activation Temperature, 40°C
Figure (3.34): Relationship between CH Consumption Rate and the Time for Different CH/GP Ratios at Activation Temperature, 80°C

3.4.6.8 SEM Images

Different images are taken to investigate the structure nature of the specimens and changes due to the hydration and the formation of the hydration products.

Figure (3.35) shows the image of the structure of the pure GP specimen hydrated for 14 days at 80°C. As shown in the figure, there is a big particle of GP surrounded with voids filled with gel formation of the C-S-H instead of the nano and very small micro particles placed in the same place before the hydration. This implies that all of these small particles have reacted and converted to a C-S-H gel formation.

Figure (3.36) shows the image of the structure of the specimen of CH/GP ratio = 20% hydrated for 14 days at 80°C. The structure here consists of big particles of GP surrounded with a thin layer of GP C-S-H. Also, its voids are filled with gel formation of GP C-S-H and some traces of CH layers lays on the GP surface.
Figure (3.35): Image of the Structure of the Pure GP Specimen Hydrated for 14 Days at 80°C

Figure (3.36): Image of the Structure of the Specimen of CH/GP ratio=20% Hydrated for 14 Days at 80°C
3.5 Applications

3.5.1 Reaction Chemical Formula

From the collected experimental data, it is possible to propose a chemical formula simulating the hydration reaction of the pure GP component and GP-CH mix. Proposing a chemical formula of the reaction helps in the numerical (computer) simulations of the GP-CH hydration. The objective of such numerical simulations is to predict different chemical and physical characteristics of the GP-blended cement hydration products outside the experimental results. Numerical simulations are particularly helpful when predicting quantities or characteristics that are difficult to acquire experimentally. These GP-CH simple hydration simulations constitute a preliminary step that will eventually lead to the complicated simulation of the GP hydration with cement. To propose the chemical formula, it is necessary to determine the maximum consumption of the GP and water for the pure GP hydration and the maximum consumption of the GP, water, and CH for the hydration of the GP-CH.

3.5.1.1 Reacted GP

Table (3.5) represents the percentage of reacted GP as a ratio of the total GP used after 14 days of hydration for the specimens activated at different temperatures of 25, 40 and 80°C. By observing this table, it is found that the maximum amount of GP consumed in the pure GP hydration is 12.5% of the total GP used. The maximum amount of GP consumed for the GP-CH hydration is 24.15% of the total GP used at the CH/GP ratio of 20%, for which all the CH amount is consumed. Hence, the actual reacted CH/GP = 0.828.
Table (3.5): Reacted GP as a Ratio of the Total GP Used after 14 days at Temperatures of 25, 40 and 80°C

<table>
<thead>
<tr>
<th>CH/GP %</th>
<th>(w/GP+CH) Ratio</th>
<th>Reacted (GP/GPJ)%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>10.71</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>12.67</td>
</tr>
<tr>
<td>20</td>
<td>0.5</td>
<td>19.66</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>19.2</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>17</td>
</tr>
</tbody>
</table>

3.5.1.2 Water Consumption

From the non-evaporable water content test, the amount of combined water due to hydration can be determined. It is found from the results that the optimum water consumption for the specimens tested after 14 days of hydration at a temperature of 80°C is 3.67% of the specimen weight for the hydration of the pure GP. However, for the GP-CH hydration, the hydration requires water of 7.23% of the specimen weight for the group of specimens with the CH/GP ratio of 20%.

3.5.1.3 Proposed Formula

According to the GP hydration models discussed earlier, the model B in Eq. 3.11 is used to simulate the hydration reaction of the pure glass powder. Hence, the model C in Eq. 3.13 is used to simulate the hydration reaction of the GP-CH. These models are used because of their simplicity and applicability in the computer simulation. The two models give only one hydration product.

Table (3.6) represents the different percentages of the main oxides of the glass powder composition and the chemical formula of the glass powder. Table (3.7) represents the different required quantities of the maximum number of moles that reacted during the hydration. These quantities include the amount of GP and the water for the pure GP.
hydration to be used in the first formula, Eq. 3.19, and the amounts of GP, CH and water used for the second formula, Eq. 3.20. The missing data is calculated from the experimental results.

### Table (3.6) Oxide Composition of the Glass Powder and Its Chemical Formula

<table>
<thead>
<tr>
<th>GP Main Oxides</th>
<th>Amount Percentage (%)</th>
<th>Molar Mass (gm/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>74.78</td>
<td>60.084</td>
</tr>
<tr>
<td>C</td>
<td>11.42</td>
<td>56.077</td>
</tr>
<tr>
<td>N</td>
<td>13.8</td>
<td>61.978</td>
</tr>
<tr>
<td>GP</td>
<td>100</td>
<td>59.84</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td></td>
<td>C_{6.1}N_{1.1}</td>
</tr>
</tbody>
</table>

### Table (3.7) Molar Quantities of the Glass Powder Hydration

<table>
<thead>
<tr>
<th>Material Quantities (Moles)</th>
<th>Pure GP Hydration</th>
<th>GP-CH Hydration</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CH</td>
<td>----</td>
<td>6.15</td>
</tr>
<tr>
<td>H</td>
<td>8</td>
<td>9.15</td>
</tr>
</tbody>
</table>

By substituting with the different missing values in the above formulas, the chemical formulas for the GP hydration can be expressed as follows:

**Pure GP hydration formula**

\[
C_{1.6}S_{6.1}N_{1.1} + 8H \rightarrow C_{1.6}S_{6.1}N_{1.1}H
\]

Eq. 3.19

C/S=0.164, H/S=1.3, and N/S=0.18

**GP-CH hydration formula**

\[
C_{1.6}S_{6.1}N_{1.1} + 6.15CH + 9.15H \rightarrow C_{7.12}S_{6.11}N_{1.1}H_{15.3}
\]

Eq. 3.20

C/S=1.17, H/S=2.5, and N/S=0.18

According to the above chemical formulas, it is observed that the formation of the GP C-S-H structure varies according to the reactant materials. For the pure GP hydration, the formed GP C-S-H has a very low C/S ratio. However, in the GP-CH hydration, the formed
GP C-S-H has a high C/S ratio because the CH provides the GP C-S-H with more Ca\(^{2+}\) atoms which increase the C/S ratio of the formed GP C-S-H gel.

### 3.6 Conclusions

This chapter consists of a theoretical and experimental investigation of the GP and GP-CH chemical and physical behaviour. Four different tests were carried out on pure GP to investigate its hydration behaviour with time at different activation temperatures. According to these tests, it is concluded that there is a slow reaction between the GP with water at a high activated temperature. The pH of the hydration solution increases with time and with increasing D.O.H.

According to the tests carried out to investigate the behaviour of the GP-CH hydration, it is concluded that the D.O.H of the specimens increases with increasing CH/GP ratio. For the same CH/GP ratio, the pH of the specimens increases with time and with increasing activated temperature. The consumption rate of the CH due to the reaction decreases with increasing CH/GP ratio. The optimum consumption of the CH/GP ratio due the reaction is around 20%. Finely ground glass powders exhibited very high pozzolanic activity. The finer the glass powder, the higher is its pozzolanic activity. According to the SEM images, it is concluded that the gel formation of the GP C-S-H fills the voids of the un-reacted big particle of the GP instead of the nano and very small micro particles placed in the same place before the hydration. This implies that all of these small particles reacted and converted to the GP C-S-H gel formation.

Two different chemical formulas for the produced GP C-S-H gel due to the pure GP and GP-CH hydration are proposed. For the pure GP hydration, the produced GP C-S-H gel has C/S=0.164, H/S = 1.3 and N/S=0.18. However, for the pure GP-CH hydration, the produced GP C-S-H gel has C/S=1.17, H/S=2.5 and N/S=0.18.
CHAPTER 4

HYDRATION AND MICROSTRUCTURE OF GLASS POWDER BLENDED CEMENT

4.1 Introduction

Glass powder, after being ground to a fineness comparable to Portland cement used in construction practice, is blended with Portland cement to produce glass powder-blended cement. The two ingredients, Portland cement and glass powder, hydrate at different rates and their reactions interact with each other. The experimental work reported in Chapter 3 was carried out to determine the hydration behaviour of the glass powder (GP) blended with CH. The positive results obtained are an indication that glass powder has pozzolanic behaviour and hence can be blended with cement. The use of glass powder with cement may improve the hydration matrix, pore solution nature and the paste microstructure. The hydration of the glass powder particles with the CH produced from the cement hydration may produce a pozzolanic form of the C-S-H that can fill the internal matrix voids. In addition, the alkalis released from the glass structure during its hydration may improve the microstructure nature of the produced paste.

This chapter is structured so that a reaction model and experimental work results are presented. The reaction model for glass powder-blended cement is proposed based on
stoichiometry calculations and different assumptions for the glass structure and the hydration nature. The pore solution nature of the cement paste and the alkalis in the pore solution are also discussed. A new pore solution model describing the alkalis distribution in the GP-blended cement matrix is developed. In the experimental part, tests are carried out to examine experimentally the behaviour of GP-blended cement. The obvious objective of the experimental program presented in this Chapter is to determine the effect of adding glass powder with different ratios on the cement paste properties.

4.2 Glass Powder-Blended Cement Hydration Modelling

In the following sections, the glass powder blended cement reaction and glass powder blended cement pore solution modelling will be presented. In addition, Portland cement pore solution and glass powder blended cement pore solution models will be discussed.

4.2.1 Glass Powder Blended Cement Reaction Modelling

It was inferred from the experimental results presented in Chapter 3 that the glass powder hydration reaction at the ambient temperature is very slow and, hence, takes a long time to occur. The hydration of the glass powder needs activation energy to initiate and continue the hydration reaction. Inside the cement hydration matrix, the hydration of cement constituents and the hydration of the glass powder do not occur simultaneously. The cement hydration starts first providing an active medium for glass powder hydration. The active medium provided by the cement hydration is represented by the associated high temperature, and high pH. In addition, as a result of cement hydration, CH is formed that will also be part of the glass powder hydration.

In this section, a proposed model that simulates the hydration reaction of the glass powder inside the cement matrix is presented. The following assumptions are considered in the hydration model:
1- The CH consumed in the glass powder hydration is a part of the CH produced from the C₃S and C₂S hydration.

2- In the glass powder chemical formula, the major oxides in the glass powder composition are considered and the minor oxides are neglected.

3- For the hydration model, Eq. 4.1, the main and only hydration product is the GP C-S-H.

4- In the glass powder C-S-H structure, there is a substitution between the Na and Si ions in bridging the tetrahedral dreirketten chain structure, which increases the C-S-H crystallinity.

5- The remaining amount of the Na ions contributes in the pore solution as alkalis, which can activate the cement hydration and the glass powder hydration as well.

Eq. 4.1 simulates the hydration model of the glass powder inside the cement hydration matrix.

\[
C_{n_{\text{c}}}S_{n_{\text{s}}}N_{n_{\text{n}}} + n_{\text{ch}}CH + n_{\text{H}}H \rightarrow n_{\text{C-S-H}}C_{a}SN_{c}H_{g}
\]  

Eq. 4.1

Where, \(n_{\text{c}}, n_{\text{s}}, n_{\text{n}}, n_{\text{ch}}\) and \(n_{\text{H}}\) are the molar quantities of the reactants, \(n_{\text{C-S-H}}\) is the molar quantity of the produced C-S-H, and \(a, c, g\) are the C/S, N/S, and H/S ratios in the C-S-H. From the molar balance calculations between the two sides of Eq. 4.1, as shown in Eq. 4.2, the C/S, N/S, and H/S ratios in the C-S-H can be obtained.

\[
\begin{align*}
\ \n_{\text{c}}^G + n_{\text{ch}} & = a \times n_{\text{C-S-H}} \\
\ \n_{\text{s}}^G & = n_{\text{C-S-H}} \\
\ \n_{\text{n}}^G & = n_{\text{nT}}^G - n_{\text{pH}}^G = c \times n_{\text{C-S-H}} \\
\ \n_{\text{H}} + n_{\text{ch}} & = g \times n_{\text{C-S-H}}
\end{align*}
\]

Eq. 4.2

where, \(n_{\text{nT}}^G\) and \(n_{\text{pH}}^G\) are the molar quantities of the sodium oxide share in the C-S-H structure and in the pore solution. From Eq. 4.2 the molar quantities \(a, c, g\) can be evaluated as follows:
There are three different cases that can be considered for the hydration behaviour of the glass powder hydration inside the cement hydration matrix. These cases are:

1. The glass powder reacts only with water with no consumption of the CH; hence \( n_\delta \) is equal to zero. From the molar balance calculations between the two sides of Eq. 4.1 due to this case, as shown in Eq. 4.4, the C/S, N/S, and H/S ratios in the C-S-H can be obtained.

\[
a = \frac{n_c^G + n_{ch}}{n_s^G} \\
c = \frac{n_n^G - n_{ps}}{n_s^G} \\
g = \frac{n_H + n_{ch}}{n_s^G}
\]

Eq. 4.3

\[
\begin{align*}
n_c^G &= a \times n_{C-S-H} \\
n_x^G &= n_{C-S-H} \\
n_n^G &= n_n^G - n_{ps} = c \times n_{C-S-H} \\
n_H &= g \times n_{C-S-H}
\end{align*}
\]

Eq. 4.4

From Eq. 4.2 the molar quantities \( a, c, g \) can be evaluated as follows:

\[
a = \frac{n_c^G}{n_s^G} \\
c = \frac{n_n^G - n_{ps}}{n_s^G} \\
g = \frac{n_H}{n_s^G}
\]

Eq. 4.5

2. The glass powder hydration consumes all the CH produced from the cement hydration. Hence, \( n_\delta = n_{CH}^p \) and the molar quantities, \( a, c, g \) and \( n_\delta \) can be calculated from Eq. 4.6.
3. The glass powder hydration consumes part of the CH produced from the cement hydration; hence, \( n_{oh} = P n^p_{CH} \).

To calculate the total amount of CH (\( n^p_{CH} \)) and C-S-H (\( n^p_{c-s-H} \)) produced due to the cement hydration, Bentz (1997) calculations of the C\(_2\)S and C\(_3\)S hydration are considered, Eq. 4.6.

\[
C_3S + (1.2 + g)H \rightarrow C_{1.7}SH_g + 1.3CH
\]
\[
C_2S + (1.2 + g)H \rightarrow C_{1.7}SH_g + 0.3CH
\]

The C/S ratio is equal to 1.7 in the conventional C-S-H. Based on the hydration model of the C\(_2\)S and C\(_3\)S, the molar quantities of the CH and C-S-H due to the hydration are shown in Eq. 4.7 and Eq. 4.8.

\[
n^p_{CH} = 1.3n_{C_3S} + 0.3n_{C_2S}
\]

\[
n^p_{C-s-H} = n_{C_3S} + n_{C_2S}
\]

**4.2.2 Glass Powder Blended Cement Pore Solution Modelling**

The pore solution of the cement paste is the liquid phase, which contains different released ions resulting from the hydration of the cement constituents. The concentration of these ions varies with time due to the hydration development and the formation of the hydration
products. The nature of the pore solution depends on different factors such as the cement type, w/c ratio, additives, mineral admixtures, and the activation energy.

It is very important to study the nature of the pore solution inside the concrete matrix due to its effect on the permeability of the concrete, whereas the liquid phase is responsible for forming the pores and channels inside the concrete matrix. The alkali-silica reaction, which deteriorates the concrete, is affected by the alkali-hydroxyl ions concentration in the pore solution (Diamond, 1975). The alkalinity of the pore solution also affects the corrosion of steel reinforcement whereas the stability of the reinforcement protective layer is improved by increasing the pore solution alkalinity around the steel bars (Lamothe, 1991). The reactivity of the mineral admixtures inside the cement paste matrix depend on the chemical composition of the pore solution (Zhou et al., 1993).

4.2.2.1 Portland Cement Pore Solution Development

For Portland cement hydrated paste, the pore solution contains different ions. The main ions are $K^+$, $Na^+$, $Ca^{2+}$, $SO_4^{2-}$, $OH^-$, $Al(OH)_4^-$, $H_2SiO_4^-$. After mixing the cement particles with water, the alkali and sulfate ions are released together into the water. The concentration of the sulfate ions starts to decrease after six hours of hydration due to the formation of the ettringite. This decrease is accompanied by an increase in the hydroxyl ions concentration in the pore solution. The concentration of the alkali ions increases rapidly in the first 24 hours to reach its maximum concentration in the pore solution within a week of the hydration. The concentration of the calcium ions in the pore solution is very low during the hydration period (Diamond, 1981; Larbi et al., 1990; Lothenbach and Winnefeld, 2006; Rothstein et al., 2002; Schafer 2004; Van Eijk 2001).

4.2.2.2 Alkalinity of Portland Cement Pore Solution

Portland cement hydration normally occurs in the presence of a limited amount of water. This fluid tends to dissolve sodium and potassium from the clinker. As a result of the ongoing hydration, alkalis become concentrated in the remaining water, which is termed "pore fluid". Longuet et al. (1973) examined pore fluid from mature pastes and observed
alkali concentrations ranging between 0.1 and 1.0%. The results (with obvious implications for hydration mechanisms and the potential for interaction of soluble alkali with aggregates in concrete) have stimulated numerous other studies that corroborate and extend pore fluid studies. These studies show that not all the alkalis are in the pore fluid: some sodium and potassium must be bound into cement paste constituents. So, the total amount of alkali ions is divided into two places. The first place is the pore solution as free ions and the second place is the cement hydration product as a substitutive material. C-S-H may contain some alkali ions in its structure as substitution of Ca ions, Richardson (2004).

4.2.2.3 Alkalinity of Glass Powder Blended Cement Pore Solution

It is expected that the alkali concentration in the pore solution of glass powder blended cement paste is greater than that of normal Portland cement paste. This is due to the fact that there is a high percentage of Na oxide in the glass powder composition. The Na ions may be released from the glass powder structure during its hydration into the pore solution. The increase of the alkali concentration in the glass-cement pore solution may be delayed until the hydration between the glass powder and the CH produced from the cement hydration starts. This is also due to the difference in the degrees of hydration of the cement and the glass powder.

The experimental work is carried out to particularly investigate the alkali concentration in the pore solution of the GP blended cement paste.

4.2.3 Portland Cement Pore Solution Models

4.2.3.1 Taylor Model (1987)

Taylor (1987) derived empirical expressions for alkali partition between solid and aqueous phases. Taylor assumed that part of the clinker alkalis stays in the pore solution and the other part is absorbed by the hydration products, especially C-S-H. The total alkali concentration in the paste is calculated using the remaining amount of alkali ions and the
volume of the solution. The amount of alkali ions released during the cement hydration is estimated using some empirical equations. The total water content in the paste and the amount of combined water in the hydration products are used to calculate the volume of the pore solution. Taylor’s model predicted the alkalis content in the pore solution and in the binding product based on two assumptions as follows:

**Alkali Release**

There are two different sources of alkali ions, which can be found in the pore solution. The first source is the cement sulfates, which provides the pore solution with its alkali ions directly after mixing with water. The proportion of these alkali ions in the pore solution depends on the sulfate content in the cement. The other source of alkali ions is the clinker. The clinker alcalis are released into the pore solution simultaneously with the hydration process.

The amount of alkali ions (Na$^+$ and K$^+$) in the cement are computed as follows in Eq. 4.9:

$$n_i^T = 2 \frac{x_i}{M_i} m^P$$  \hspace{1cm} \text{Eq. 4.9}

where, $n_i^T$ is the moles of alkali ions $i$ (K$^+$ or Na$^+$) in the cement; $x_i$ is the mass fraction of the alkali oxide $i$ in the cement and $m^P$ is the mass of Portland cement.

The moles of the alkali ions existing in the cement sulfates are calculated as follows in Eq. 4.10:

$$n_i'^{\text{sulf}} = f_i'^{\text{sulf}} n_i^T$$  \hspace{1cm} \text{Eq. 4.10}

where, $n_i'^{\text{sulf}}$ is the amount of alkali ions in the cement sulfates and $f_i'^{\text{sulf}}$ is the mass fraction of the alkali oxide $i$ in the sulfate ($0 \leq f_i'^{\text{sulf}} \leq 1$).

Taylor (1990) determined the $f_i'^{\text{sulf}}$ value by following the procedure enumerated below:

1- Calculating two different ratios as follows, Eq. 4.11:
where \( n_s^T \) is the moles of sulfate in clinker, which equals \( \frac{x_s}{M_s} \).

2. If \( R_s \leq 0.8 \) and \( \chi < 3.67, f_{K,\text{sm}} = 1.12 R_s \) and \( f_{N,\text{sm}} = 0.56 R_s \).
3. If \( R_s > 0.8 \) and \( \chi < 3.67, f_{K,\text{sm}} = 0.9 \) and \( f_{N,\text{sm}} = 0.56 R_s \).
4. If \( \chi = 3.67, R_s \leq 0.8, \quad f_{K,\text{sm}} = 1.12 R_s \left( n_k^T + n_n^T \right) / \left( 1.12 n_k^T + 0.56 n_n^T \right) \) and \( f_{N,\text{sm}} = 0.56 R_s \left( n_n^T + n_k^T \right) / \left( 1.12 n_k^T + 0.56 n_n^T \right) \).
5. If \( \chi = 3.67, R_s > 0.8, \quad f_{K,\text{sm}} = 0.9 \left( n_k^T + n_n^T \right) / \left( 1.12 n_k^T + 0.56 n_n^T \right) \) and \( f_{N,\text{sm}} = 0.56 R_s \left( n_n^T + n_k^T \right) / \left( 1.12 n_k^T + 0.56 n_n^T \right) \).

The amount of alkalis \( n_{i,\text{clink}} \) in each clinker phase (C\(_3\)S, C\(_2\)S, C\(_3\)A and C\(_2\)AF) is calculated using Eq. 4.12.

\[
 n_{i,\text{clink}} = \left[ \sum_{j=1}^{4} f_{i,j} \left( 1 - f_{i,\text{sat}} \right) a_j \right] \times n_i^T \tag{Eq. 4.12}
\]

where \( j \) is the clinker phase; \( f_o \) the fraction of alkali ion in each phase; \( a_j \) is the degree of hydration of each phase.

The fraction of alkali ion \( f_o \) in the clinker phases is presented in Table 4.1 (Taylor, 1987b).

**Table 4.1:** The Fraction of Alkali Ions in Individual Clinker Phases to the Amount of Non-Sulfate Alkali Ions in Clinker (Taylor, 1987b).

<table>
<thead>
<tr>
<th>Alkali content</th>
<th>Na(_2)O</th>
<th>K(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite</td>
<td>0.44</td>
<td>0.29</td>
</tr>
<tr>
<td>Belite</td>
<td>0.17</td>
<td>0.41</td>
</tr>
<tr>
<td>Aluminate</td>
<td>0.36</td>
<td>0.27</td>
</tr>
<tr>
<td>Ferrite</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>
The total amount of alkali ions released by the cement hydration is calculated as follows in Eq. 4.13:

\[ n_i^r = n_i^{\text{total}} + n_i^{\text{clink}} = \left[f_i^{\text{total}} + \sum_{j=1}^{n^d} f_{ij} \left(1 - f_i^{\text{total}}\right) \chi_j \right] \times n_i^T \]  

Eq. 4.13

**Alkali Binding**

As mentioned earlier, the total released alkali ions \( n_i^r \) are divided into two parts, the pore solution and the hydration products, yielding:

\[ n_i^r = n_i^b + n_i^s \]  

Eq. 4.14

where, \( n_i^b \) is the amount of the alkali ions bound in the hydration products and \( n_i^s \) is the amount of alkali ions in the pore solution, which is equal to:

\[ n_i^s = C_i V_w \]  

Eq. 4.15

in which \( C_i \) is the concentration of the alkali ions \( i \) (mol/L) and \( V_w \) is the volume of the pore solution.

Taylor (1987b) assumed that the amount of the bound alkali ions is proportional to the concentration of pore solution and the amount of the hydration products; i.e.,

\[ n_i^b = b_{i,j} C_i F \]  

Eq. 4.16

where, \( b_{i,j} \) is the binding factor of the alkali \( i \) and \( F \) is the fraction between the quantity of the hydration products.

Substituting Eqs 4.15 and 4.16 into 4.17, the alkali concentration in the pore solution is calculated as:

\[ C_i = \frac{n_i^r}{V_w + b_{i,j} F} \]  

Eq. 4.17
Brouwers and Van Eijk (2003) further developed the method proposed by Taylor (1987b). They assumed that the only hydration product, which can bind the alkali ions, is the C-S-H. They proposed the amount of alkali ions bound in the C-S-H to be:

\[ n_i^b = R_{d,i} C_i m_{c-s-H} \]  

Eq. 4.18

in which \( m_{c-s-H} \) is the mass of the C-S-H in the solids and \( R_{d,i} \) is the distribution ratio of the alkali \( i \), which is defined as the ratio between the alkali in solid C-S-H (mmol/gm) over the alkali concentration in the solution (mmol/mL). All calculations are based on the fact that 100gm of cement hydrates to form 80gm of C-S-H. Brouwers and Van Eijk (2003) made use of the results of the experiments carried out by Hong and Glasser (1999) to compute the C-S-H binding factors of alkalis. These factors are:

\[ R_{d,N} = 0.39 \]
\[ R_{d,K} = 0.25 \]

From the previous relations, Eq. 4.16 to Eq. 4.18, the alkali concentration in the pore solution can be solved according to Eq. 4.19.

\[ C_i = \frac{n_i^f}{V_s + R_{d,i} m_{c-s-H}} \]  

Eq. 4.19

in which \( n_i^f \) is computed from Eq. 4.13. The parameters in Eq. 4.18 and Eq. 4.19, \( a_s, m_{c-s-H} \), and \( V_s \), can be calculated using the CEMHYD3D model.

**4.2.4 Glass Powder–Blended Cement Pore Solution Models**

This section presents a model that is developed by modifying the model proposed by Taylor (1987b). The developed model is able to describe the alkali ions distribution of the glass powder blended cement pastes.
Alkali release

In the case of using glass powder blended cement, there are three sources of alkali ions in the pore solution. The first two sources are the cement sulfates and the clinker phases, as described in Eq. 4.20 and 4.21. The third source of alkali ions is the glass powder, which contains about 13% of sodium oxide of its weight. Eq. 4.22 represents the amount of alkali ions in the hydrated glass powder.

\[ n_i^{\text{cement}} = f_i^{\text{cement}} n_i^{T,p} \]  
Eq. 4.20

\[ n_i^{\text{clinker}} = \sum_{j=1}^{4} f_{ij} \left(1 - f_i^{\text{cement}} \right) n_j^{T,p} \]  
Eq. 4.21

\[ n_i^{G} = a_G n_i^{T,G} \]  
Eq. 4.22

Here, \( n_i^{T,p} \) is the amount of alkalis in the Portland cement, \( n_i^{G} \) is the moles of alkalis released from the glass powder, \( a_c \) is the glass powder degree of hydration and \( n_i^{T,G} \) is the total amount of alkalis in the glass powder.

The total amount of alkali ions released by the glass powder blended cement hydration is:

\[ n_i' = n_i^{\text{cement}} + n_i^{\text{clinker}} + n_i^{G} \]  
Eq. 4.23

\[ n_i' = f_i^{\text{cement}} + \sum_{j=1}^{4} f_{ij} \left(1 - f_i^{\text{cement}} \right) n_j^{T,p} + a_G n_i^{G} \]  
Eq. 4.24

Alkali Binding

As previously mentioned, the total amount of released alkali ions are divided into two parts, the pore solution and the hydration products, yielding:

\[ n_i' = n_i^{P} + n_i^{T} \]  
Eq. 4.25
where, $n^i$ is the amount of alkali ions bound in the hydration products; $n^i_0$ is the amount of alkali ions in the pore solution, which is a function of the alkalis concentration in the pore solution and the volume of the pore solution, as described in Eq. (4.26).

$$n^i_0 = C_i V_w$$  \hspace{1cm} \text{Eq. 4.26}

For the binding alkalis, there are two different hydration products that contain alkali ions, which are the cement hydration C-S-H and the GP C-S-H. Eq. 4.27 represents the amount of binding alkalis as following:

$$n^b_i = C_i \left( R_{d,i} m_{c-s-H}^i + R_{d,G} m_{c-s-H}^G \right)$$  \hspace{1cm} \text{Eq. 4.27}

in which $m_{c-s-H}^G$ is the mass of C-S-H produced due to the glass powder hydration and $R_{d,G}$ is the distribution ratio of the alkali $i$, which is defined as the ratio between the alkali in the GP C-S-H (mmol/gm) over the alkali concentration in the solution (mmol/mL).

From the last two equations, Eq. 4.26 and 4.27, the alkali concentration in the pore solution can be solved according to the following equation.

$$C_i = \frac{n^i_0}{V_w + R_{d,i} m_{c-s-H}^i + R_{d,G} m_{c-s-H}^G}$$  \hspace{1cm} \text{Eq. 4.28}

In which $n^i_0$ is computed using Eq. (4.25). The parameters in Eq. 4.27 and Eq. 4.28, $\alpha$, $m_{c-S-H}$, $m_{c-s-H}^G$, and $V_w$, can be calculated using the MOD-model, which numerically simulates the glass powder blended cement hydration.

### 4.3 Experimental Program

#### 4.3.1 Introduction

The main objective of this experimental work is to investigate the glass powder blended cement paste behaviour due to different addition ratios of glass powder. Another objective
of this work is to determine the physical and chemical characteristics changes of the cement paste due to the GP addition. A regression model for the CH amount consumed due to the glass powder hydration in the cement matrix as a function of the CH produced from the cement hydration and other parameters is developed based on the experimental results. The obtained information will be used in the computer simulation of the GP cement hydration process.

Five different tests were carried out to evaluate the hydration behaviour of the GP-blended cement. These tests are:

1. Non-evaporable water content test,
2. pH test,
3. Pore solution alkalinity due the Na release during the hydration,
4. XRD tests investigating the CH consumption by the GP with time, and
5. Chemical shrinkage test.

In addition, SEM images were taken to monitor the microstructure changes of the hydration matrix with time.

The following sections describe the methodology and the purpose of the tests, the analysis of the results, the simulation of the GP and CH reaction in the cement hydration matrix, a regression model for the consumed CH, and finally the conclusion of the experimental work presented in this chapter.

4.3.2 Materials

4.3.2.1 Glass Powder

The glass powder used is the same as that used in the experimental work in Chapter 3. This glass powder has a maximum particle size of 100 µm and specific surface area of 1.72m²/g.
4.3.2.2 Ordinary Portland Cement

The Portland cement used is Type10, according to ASTM C150 (2005). The different physical and chemical properties of the Portland cement used are represented in Tables (4.2 and 4.3).

**Table 4.2 The Physical Properties of the Used Portland Cement**

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Gray</td>
</tr>
<tr>
<td>Density</td>
<td>3.14</td>
</tr>
<tr>
<td>Specific Surface</td>
<td>Blaine 354m²/kg</td>
</tr>
<tr>
<td></td>
<td>BET   2.6m²/g</td>
</tr>
<tr>
<td>Granulometry</td>
<td>Dₜ₀=17µm</td>
</tr>
<tr>
<td>Morphology</td>
<td>Angular Particles</td>
</tr>
</tbody>
</table>

**Table 4.3 The Chemical Composition of the Used Portland Cement**

<table>
<thead>
<tr>
<th>Chemical Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (S)</td>
</tr>
<tr>
<td>Al₂O₃ (A)</td>
</tr>
<tr>
<td>Fe₂O₃ (F)</td>
</tr>
<tr>
<td>CaO (C)</td>
</tr>
<tr>
<td>MgO (M)</td>
</tr>
<tr>
<td>TiO₂ (T)</td>
</tr>
<tr>
<td>K₂O (K)</td>
</tr>
<tr>
<td>Na₂O (N)</td>
</tr>
<tr>
<td>SO₃ (S)</td>
</tr>
<tr>
<td>PF</td>
</tr>
</tbody>
</table>

4.3.3 Parameters Studied

In this work, three main groups of specimens are cast with a total number of 105 specimens. The quantity of Portland cement used is constant for all the cast specimens. The addition of the GP is a ratio of the cement weight. These additions are 0, 5, 10, 15, 20, 25, 30% of the cement weight. The chosen GP ratios are varied to examine the effect of low and high addition ratios of GP on the physical/chemical characteristics of the cement hydration pastes. The activation temperature is also a parameter. Three different temperatures were chosen, which are 25, 40, 80°C for the hydration reaction of the GP blended cement. The water/solid (w/s) ratio is 0.5 for all cast specimens. The specimens were tested at 0, 1, 3, 7, 14, 28 days after casting. Table (4.4) represents the different parameters in this experimental part.
4.3.4 Preparation of Test Specimens

The different groups were cast at room temperature 25 °C. The solid materials and water were mixed together using a food mixer for three minutes to make sure that all the materials are mixed well. The specimens were cast in 15ml secured plastic tubes to make sure that no water evaporation can occur during the hydration. Each group of specimens was then put at its activated temperature for the limited time of testing.

Four different steps are followed to prepare the specimens for testing. First, the specimens were released from the cast tubes to be ground. The specimens were then dried for 24hr in a drier at 10°C to remove all the free water. Afterwards, the specimens were ground again and sieved to obtain a powder of maximum particle size of 100µm. Then the specimens were stored in secured tubes until the time of testing.

Table (4.4): The Different Parameters Used in the Experimental Work

<table>
<thead>
<tr>
<th>Groups</th>
<th>Cement Addition Ratio (%)</th>
<th>GP Addition Ratio (%)</th>
<th>GP/C Ratio (%)</th>
<th>Water/Solid Ratio</th>
<th>Activation Temperature</th>
<th>Testing Time (Days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>25 °C</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>5</td>
<td>5</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
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<td>90</td>
<td>10</td>
<td>10</td>
<td></td>
<td></td>
<td>3</td>
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<tr>
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<td>13</td>
<td>15</td>
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<td>7</td>
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<td>77</td>
<td>23</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>40 °C</td>
<td>0</td>
</tr>
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<td>5</td>
<td>5</td>
<td></td>
<td></td>
<td>1</td>
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<td>90</td>
<td>10</td>
<td>10</td>
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</tr>
<tr>
<td>III</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>80 °C</td>
<td>0</td>
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<td>77</td>
<td>23</td>
<td>30</td>
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</tr>
</tbody>
</table>
4.3.5 Testing

Four different tests were carried out on the powder specimen to investigate the complete chemical and physical behaviour of the GP-blended cement hydration reaction. Details of these tests are given in the following sections.

4.3.5.1 Determination of Degree of Hydration Using Non-Evaporable Water Content

As mentioned previously in Chapter 3, this test can determine the consumed water in the GP-blended cement hydration. Certain powder amount of weight of two (2) gm was placed in an oven at 1010°C to release all the combined water. Then the specimen was weighed to determine the weight loss due to the evaporation of the combined water. The non-evaporable water content $w_n$ is calculated using Eq. 4.29 as follows:

$$w_n = \frac{w_i - w_s}{w_s}$$  \hspace{1cm} \text{Eq. 4.29}

in which $w_i$ is the weight of the specimen before being placed in the oven and $w_s$ is the specimen weight after losing the combined water.

4.3.5.2 pH

According to specification ASTM D1293 (2005), the pH test was carried out for the specimens using a "HACH ONE pH METER" at Soil Mechanics Laboratory, Civil Engineering Department, University of Sherbrooke, as shown in Figure (3.4), to determine the alkalinity of the specimens at different times during and after the hydration. The hydration degree of the GP is affected by the pH value of the cement medium around it. pH measurements indicate the alkalinity of the pore solution of the hydrating system.
4.3.5.3 Na Concentration

It is expected that the reactivity of the cement and glass powder hydration as well may be affected by the alkalis concentration in the pore solution. After mixing the GP-blended cement with water, Na ions can be released from the glass powder into the pore solution. This alkalinity nature of the pore solution can activate the GP hydration and the cement hydration as well.

One gram of the specimen powder is mixed with 100ml of distilled water. The mixture was then boiled for half an hour to make sure that all the alkali ions are dissolved in the solution. Afterwards, the solution was filtered in 300ml distilled water to obtain a clear solution without solids. According to the ASTM-C441(2005), the “PERKIN ELMER-AAAnalyst 300” flame photometry apparatus at Environmental Laboratory was used, Civil Engineering Department, University of Sherbrooke, as shown in Figure (3.5), to measure the Na concentration in the tested solution.

4.3.5.4 X-Ray Diffraction (XRD) Analysis

The XRD analysis is used in this work as an approximate way to calculate the amount of CH crystals in the powder. These CH crystals are produced during the cement hydration as one of the hydration products. The CH crystals have known peak positions at $2\theta=18, 28$ and $34^\circ$. The amount of CH in any compound can be approximately determined by making the appropriate comparison of CH peak intensities of other compound where both the CH amount and the CH peak intensities are known. This is done using a constant CH amount/CH peak intensity ratio.

4.3.5.5 Chemical Shrinkage

This section includes testing of the chemical shrinkage for nine different glass powder cement pastes. These pastes are cast with three different w/s ratios of 0.4, 0.5, and 0.6 and GP/C ratios of 0, 10, and 20% hydrated at temperature of 25°C.
Experimental test

Le Chatelier (1904) presented a very simple method for testing the chemical shrinkage of cement pastes. As shown in Figures (4.1 and 4.2), the test is carried out by filling a 100ml flacon with high vertical collar with a fresh cement paste up to the base of the collar. Then, the paste is covered with a certain volume of water. The evaporation of the water is prevented by putting a spot of oil on the top surface of the water. During the cement hydration, the total volume of paste decreases and the water penetrates the paste. The difference between the initial level of water and that after (t) time is measured to determine the shrinkage volume of the paste due to the hydration. The chemical shrinkage measurements are taken every hour for the first 24 hours of pouring the paste and then every 24 hours for the remaining period of testing of 200 hours. By determining the paste weight and the volume loss of the water in the collar, the chemical shrinkage of the paste can be obtained in (ml/gm-cement) as follows:

\[
SH_{ch} = \frac{\Delta V}{W_{paste}}
\]

Eq. 4.30

where, \(SH_{ch}\) is the chemical shrinkage of the paste (ml/gm-cement) at any time \(t\), \(\Delta V\) is the water volume loss (ml) measured at any time \(t\), and \(W_{paste}\) is the paste weight (gm). As mentioned earlier, nine paste samples with w/s ratios of 0.4, 0.5, and 0.6 and GP/C ratios of 0, 10, and 20% were tested to measure the chemical shrinkage with time.
The level of the cement paste in the flacons

Before

After

$\Delta V =$ volume of water that penetrated the paste

Figure (4.1): Method of Testing the Chemical Shrinkage for Cement Pastes According to Le Chatelier (1904)

Figure (4.2): Method of Testing the Chemical Shrinkage for Cement Pastes
4.3.6 Analysis of Results

4.3.6.1 Introduction

The following sections present the chemical and physical behaviour development of the glass powder-blended cement hydration with time. The experimental results represent the effect the different GP addition ratios on the degree of hydration, pH, Na concentration in the pore solution of the produced paste. XRD analysis was carried out to determine the amount of the CH in each paste. Finally, some SEM images were taken for the GP-blended cement specimens before and after hydration to indicate the microstructure changes due to the hydration.

4.3.6.2 Degree of Hydration

In this part, the D.O.H. is calculated for the different glass powder blended cement specimens as a ratio between the actual non-evaporable water content at any time and the total non-evaporable water content of the complete hydration cement, which equals 0.24. The degree of hydration of the glass powder-blended cement was calculated from the test as follows:

\[
D.O.H = \frac{(w_n)}{(w_n)_{c_{\text{max}}}} = \frac{(w_n)}{0.24}
\]

where D.O.H. is the degree of hydration of any specimen at certain testing time and certain activation temperature, \((w_n)\) is the non-evaporable water content of any specimen at certain testing time and certain activation temperature and \((w_n)_{c_{\text{max}}}\) is the maximum non-evaporable water content of cement hydration.

Figures (4.3 to 4.5) show the relationships between the D.O.H. of the different specimens hydrated at different temperatures, namely 25, 40, 80°C and the GP/C ratio. For all the tested groups, there is no noticeable increase in the D.O.H. due to the different additions of GP. This may be explained by the large difference between cement degree of hydration and
the GP degree of hydration. The D.O.H. of the GP is very slow and low as compared with the D.O.H. of the cement. For the specimen groups hydrated at temperatures 25 and 40°C, it is found that the increase in the D.O.H. due to increasing the GP/C ratio may appear after 7 days of hydration. However, for the specimens hydrated at 80°C, the effect of the GP hydration on the total D.O.H can be observed after 3 days of hydration. This means that the activation temperature has a great effect on the GP hydration inside the cement hydration matrix. The activation temperature is not the only factor affecting the GP hydration but also the maximum particle size, the particle size distribution of the used GP and the rate of producing the CH during the cement hydration also affect the reactivity of the GP.

Figure (4.3): Relationships between D.O.H. and GP/C Ratio at Different Dates at Temperature, 25°C
Figure (4.4): Relationships between D.O.H. and GP/C Ratio at Different Dates at Temperature, 40°C

Figure (4.5): Relationships Between D.O.H. Versus GP/C Ratio at Different Dates at Temperature, 80°C
4.3.6.3 pH

pH gives an indication of the degree of alkalinity of the tested material. For all the glassy composition materials, there is no reactivity if the surrounded pH < 9, (Paul 1977). The hydration of the GP release alkali ions in the pore solution, which may increase the overall pH of the hydration matrix.

Figures (4.6 to 4.8) show the relationship between the pH and the GP/C ratio for all the specimen groups. For all the tested groups, it is found that there is a slight increase in the pH by increasing the GP/C ratio. The pH increases by 10% due to increasing the GP/C ratio by 30% for the specimens hydrated at the same temperature and tested after the same period. However, for the same GP/C ratio, the pH increases by 20% during 28 days of hydration as shown in Figures (4.9 to 4.11).

![Figure (4.6): Relationships between pH and GP/C Ratio at Different Dates at Temperature, 25°C](image)

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Figure (4.7): Relationships between pH and GP/C Ratio at Different Dates at Temperature, 40°C

Figure (4.8): Relationships between pH and GP/C Ratio at Different Dates at Temperature, 80°C
Figure (4.9): Relationships between pH and the Time for Different GP/C Ratios at Activation Temperature, 25°C

Figure (4.10): Relationships between pH and the Time for Different GP/C Ratios at Activation Temperature, 40°C
4.3.6.4 Alkalis in Pore Solution

This part presents the Na concentration in the pore solution for the different GP/C specimens. Figures (4.12 to 4.14) show the relationship between the Na percentage in the pore solution and time for all the specimens. It is found that the main increase in the Na concentration occurs during the first 3 days of hydration. Afterwards, it tends to be constant with time. The Na concentration increases by increasing the GP/C ratio and the hydration temperature during the hydration period. At a hydration temperature of 80°C, the Na concentration in the pore solution for the specimen of GP/C=30% increases 2 times as that for the specimen of GP/C=5% after 28 days of hydration. This means that the Na ions are released from the GP during its hydration. These alkali ions can activate the hydration reaction of the C2S and C3S and the hydration of the GP as well. The microstructure of the produced paste may also be improved due to the precipitation of the Na ions on the surface of the C-S-H, which improves the ionic distribution and the density of the produced paste.
Figure (4.12): Relationships between (Na)% and Time for Different GP/C Ratios at Activation Temperature, 25°C

Figure (4.13): Relationships between (Na)% and Time for Different GP/C Ratios at Activation Temperature, 40°C
4.3.6.5 X-R-D Analysis

All the specimens are analysed using XRD in certain zones of $2\theta = 16^\circ$ to $2\theta = 36^\circ$. These zones are chosen to cover the CH peaks zone, which exist at $2\theta = 18^\circ$, $28^\circ$, and $34^\circ$ to determine the CH content of different specimens with time. Figure (4.15) shows a $2\theta$-intensity relationship curve for the plain cement paste. As can be seen, there are different peaks that may appear in the tested zone between $2\theta = 16^\circ$ to $36^\circ$. The peaks at $2\theta = 18^\circ$, $28^\circ$, and $34^\circ$ are the CH crystalline peaks and the peaks at $2\theta = 20^\circ$, $32^\circ$ and $33^\circ$ are for different types of C-S-H gel forms. The peak at $2\theta = 29^\circ$ is for the calcite which maybe formed during the specimens preparation due to the reaction between the CH in the cement paste and the atmospheric C$_2$O.
Figure (4.15): $2\theta$-Intensity Relationship for General Cement Paste

Figure (4.16) shows the $2\theta$-intensity relationships for the plain specimens during a hydration period of 28 days at an activation temperature of 80°C. The figure also shows the production of the CH with time due to the cement hydration. It can be seen that the CH peak intensities increase with time due to the continuation of the cement hydration. Figure (4.17) shows the CH production as a ratio of the maximum CH amount produced at 28 days for the plain cement specimens hydrated at 80°C. The CH production rate is calculated by dividing the CH peak intensity value at $2\theta = 18^\circ$ at any time (t) over that peak value at 28 days. It is found that about 80% of the produced CH after 28 days of hydration is produced after the first three days of hydration. The $2\theta$-intensity relationship development for the different GP-blended cement specimens hydrated at 80°C is shown in Figure (4.18). It can be observed that the CH peak intensity values decrease with an increase in the GP/C ratio.
Figure (4.16) 2θ-Intensity Relationship for GP/C Ratio=0% at Different Dates at Activation Temperature, 80°C

Figure (4.17): Production of the CH Rate versus Time for the Plain Cement Paste at Activation Temperature, 80 °C
Figure (4.19) shows the maximum CH consumption rate after 28 days of hydration for all GP/C ratio specimens hydrated at 25, 40, 80°C as a function of the total CH produced in the plain pastes. The maximum CH consumption rate is calculated as follows:

$$\text{CH consumption rate} = \left[ 1 - \frac{I_i}{I_0} \right] \%$$

where, $I_i$ is the CH peak intensity value at $2\theta = 18^\circ$ at 28 days for the paste of GP/C = $i$ and $I_0$ CH peak intensity value at $2\theta = 18^\circ$ at 28 days for the paste of GP/C = 0%.

This ratio is calculated for all the specimens hydrated at 25, 40, 80°C.

As shown in the figure, the CH consumption increases by increasing the GP/C ratio. For specimens hydrated at 80°C, the main CH consumption rate for the pastes of GP/C ratio of 10% is equal to 35%. By increasing the GP/C ratio to more than 10%, there is a little increase in the CH consumption by increasing the GP addition. This means that a GP/C ratio of 10% can be considered as the optimum ratio and can hence be recommended.

### 4.3.6.6 Chemical Shrinkage

Figures (4.20 to 4.22) show the relationships between the chemical shrinkage and time for the pastes of w/s ratios 0.4, 0.5, and 0.6 hydrated at temperature of 25°C. As shown in the figures, the chemical shrinkage increases with time. By increasing the GP/C ratio, the chemical shrinkage decreases with time. For every w/s ratio, it is noted that the chemical shrinkage values for the different pastes of GP/C ratios of 0, 10, and 20% for the first 24 hours are almost the same. After that, these values differ and the effect of adding the glass powder appears to decrease the chemical shrinkage values of the pastes with time. This can be explained by the fact that, in the early ages, the hydration of the glass powder and its conversion to GP C-S-H takes more time than the hydration of cement. Hence, the chemical shrinkage is not affected by the glass powder addition in the paste. With time, the glass-powder hydration products fill the paste voids, which are formed during the cement hydration. This can decrease the total volume loss of the paste due to the hydration. In
addition, not all the glass powder amounts are converted to hydration products. More than 50% of the glass powder, depending on its fineness, remain unchanged (without hydration), which can control the chemical shrinkage of the paste.

Figure (4.18): 2θ-Intensity Relationship for Different GP/C Ratios at 28 Days of Hydration at Activation Temperature, 80°C
Figure (4.19): Relationships between CH Consumption Rate and GP/C Ratio at 28 Days of Hydration at Different Activation Temperature 25, 40, and 80°C

Figure (4.20): Relationships between the Chemical Shrinkage Results and the Time for All the Pastes of w/s=0.4
Figure (4.21): Relationships between the Chemical Shrinkage Results and the Time for All the Pastes of w/s=0.5

Figure (4.22): Relationships between the Chemical Shrinkage Results and the Time for All the Pastes of w/s=0.6
4.3.6.7 SEM Image

Different images are taken to investigate the microstructure development for the different GP/C specimens. Figure (4.23) shows the image for the plain cement paste microstructure hydrated for 28 days at 80°C. As shown in the figure, there are CH crystals surrounded by a C-S-H gel. Figures (4.24 and 4.25) show the image of the microstructure of the specimens of GP/C ratios of 20 and 30% hydrated for 28 days at 80°C. The figures show that the C-S-H microstructure is in contact with the CH crystals. It is shown that the C-S-H structure is well distributed in the cement matrix and is denser than that in the plain paste.

By comparing the microstructure of the pastes in Figures (4.23, 4.24, and 4.25), it is observed that there is a difference in the C-S-H gel microstructure between the GP blended cement paste and plain cement paste. The gel formation in the GP blended cement paste is denser and more coherent than that in the plain pastes. The hydration of the GP inside the cement hydration matrix may produce a dense matrix and improve the durability properties of concrete in which it is incorporated.

Figure (4.23): SEM Image of the Structure of the Plain Cement Paste Hydrated for 28 Days at 80°C
Figure (4.24): SEM Image of the Structure of the Specimens with GP/C Ratio = 20% Hydrated for 28 Days at 80°C

Figure (4.25): SEM Image of the Structure of the Specimens with GP/C Ratio = 30% Hydrated for 28 Days at 80°C
4.4 Applications

4.4.1 CH Consumption

To simulate the hydration of the GP inside the cement matrix, two different requirements are needed. The first requirement is the exact amounts of the reactants, GP, CH and water to create the chemical formula of the reaction. This formula is already obtained in Chapter 3. The second requirement is the CH consumption ratio due to the hydration of the GP with time. In this part, according to the experimental results, an equation, Eq. 4.33, that describes the CH consumption due to the GP hydration, is proposed. This equation correlates the GP/C ratio, time and activation temperature. Eq. 4.33 predicts the CH consumption due to the GP hydration as a ratio of the total CH produced during the cement hydration with time.

A linear regression model was developed based on the experimental results to develop an expression for computing the CH consumption due to the GP hydration as a ratio of the total CH produced due to the cement hydration \( n_{CH} \) as a function of the GP/C ratio \( R_{GP} \), time \( t \) and the activation temperature \( T \). The formula can be assumed in the following form:

\[
 n_{CH} = f(R_{GP}, t, T)
\]

where \( n_{CH} = \frac{CH\ Concumed}{CH\ Produced} \% \), \( R_{GP} \) is the glass powder-cement ratio (\%), \( t \) is the time (days) and \( T \) is the activation temperature (\degree C).

The following expression given is determined as a best fit.

\[
 n_{CH} = 0.012 R_{GP} (T + 1.06t) + 0.00655(T \times t)
\]

Eq. 4.33

This equation is meant for the glass powder-blended cement pastes activated at temperatures between 25 to 80\degree C. In order to examine the model, the experimental results of the CH consumed and the theoretical results, from Eq. 4.33, were plotted for all the specimens in
Figure (4.26). The plot indicates the agreement between the suggested model and the experimental results.

\[ n_{CH} = 0.012R_{GP}(T+1.06t) + 0.00655(T\times t) \]

\[ R^2 = 0.96 \]

Figure (4.26): Theoretical versus Experimental \( n_{CH} \) for All the Specimens

4.5 Conclusion

The hydration characteristics of GP blended cement are theoretically and experimentally studied in this chapter to investigate the effect of adding the GP in the cement matrix. The chapter includes two different parts: the first part includes different possible theoretical models of the GP hydration in the cement hydration matrix. A pore solution model for the GP blended cement is also proposed based on the original (Taylor, 1987b) and later (Brouwers and Van Eijk, 2003) theories for the linear partition of alkali ions in the solid and aqueous phases in hydrated cement paste. The second part includes an experimental study of the chemical and physical characteristics of the GP blended cement pastes. Based on the experimental results and the discussions presented, several conclusions can be drawn:
1- According to the proposed models for the GP blended cement pore solution, the development of the pore solution composition of hydrated GP blended cement paste can be predicted.

2- The pH of the specimens increases with an increase in the GP/C addition ratio with time.

3- The consumption rate of the CH increases with time. It is also concluded that this rate increases with an increase in the activated temperature.

4- The consumption rate of the CH due to the GP hydration increases with an increase in the GP/C ratio.

5- The maximum consumption of the CH due to the reaction with the GP is about 50% of the total amount of the CH produced due to the cement hydration.

6- The Na concentration in the pore solution increases 3 times when the GP/C ratio is increased from 0% to 30%.

7- It was obvious from the SEM images that the C-S-H gel formation in the GP blended cement paste is denser and more coherent than that in the plain pastes.

8- The model that describes the CH consumption due to the GP hydration in the cement hydration matrix agrees reasonably well with the experimental results.
CHAPTER 5

COMPUTER MODELLING OF GLASS POWDER BLENDED CEMENT

5.1 Introduction

Most of the experimental research investigations done on glass powder concrete have been focusing on determining the changes in the mechanical properties of the concrete as a result of adding glass powder to the mix. Conducting experiments in the area of determining the effect of the glass powder on the chemical and the physical properties of the concrete is not actually always an easy task. This fact is attributed to the scarce experimental research investigation in this area. These experimental investigations aim at determining properties such as chemical shrinkage, conductivity, pore solution composition, porosity, amount of released ions with time, degree and heat of hydration with time, etc. Carrying out these experiments is in fact time consuming and relatively costly. Determining these properties using computer simulations may save the effort and time of experiments. This fact substantiates the need for reliable computer simulations of these experiments that will definitely save time, effort and indeed, money.

As mentioned in previous chapters, a major objective of this research work is to simulate numerically glass powder hydration inside a cement matrix. This objective can be achieved by developing a new computer model that incorporates the glass powder hydration in the CEMHYD3D computer model. This model is called the MOD-model, which simulates the
hydration of glass powder blended cement. Different computer implementations (runs) of the MOD-model for different glass powder additions are carried out to assess the model.

The data required to execute the computer simulations are collected based on the extensive experimental program results detailed Chapters 3 and 4. The collected data, the chemical and physical properties of the glass powder and the hydration reaction details of the glass powder with the CH inside the cement hydration matrix, are used in these computer simulations to model glass powder cement hydration.

The following sections include information about the glass powder reactivity and the different factors affecting it. Computer modelling details and the inputs and outputs of the MOD-model are discussed in detail. The differences between the MOD-model and CEMHYD3D model results due to the glass powder hydration incorporation are also discussed.

5.2 Reactivity of Glass Powder

The hydration of glass powder is an essential parameter, which has to be considered when simulating the reaction of glass powder in cement, as mentioned in Chapter 3 and 4. It depends among other factors on the intrinsic reactivity of the glass powder. It is difficult to determine exactly the reactivity rate of the glass powder in the cement due to the several factors affecting the reactivity. These factors include the presence of crystalline minerals, chemical composition, geometrical characteristics, temperature, glass structure and the alkaline environment.

5.2.1 Methods to Characterize Reactivity

Several methods are used to determine the reactivity of a glass material such as slag and glass powder. These methods include strength development, reaction degree, water retention, and the CH consumption methods. In this research work, the last three methods are carried out experimentally.
5.2.1.1 Water Retention

The amount of combined water in the hydrating glass powder cement pastes is used to evaluate the glass powder reactivity in the cement matrix. The determination of the amount of water consumed due to the hydration of the GP-CH and glass powder blended cement in a certain period of time is described in detail in Chapter 3 and Chapter 4. Increasing the amount of the combined water in the GP-CH hydrated paste gives an indication of the reactivity of the glass powder.

5.2.1.2 Reaction Degree

The reaction degree of the glass powder at a given age is the most direct output result, which accounts for the glass powder reactivity. It is defined as the proportion of glass powder that reacts at a certain age to the total amount of glass powder used at the beginning. The determination of the amount of the glass powder consumed due to the hydration of the GP-CH and glass powder blended cement with time is described in detail in Chapter 3 and Chapter 4. The advantage of using this factor to evaluate the reactivity of the glass powder is that it directly gives the quantity of glass powder that already reacted.

5.2.1.3 CH Consumption

The amount of CH consumed in the hydration of the glass-powder cement pastes is used to evaluate the glass powder reactivity in the blended cement. The determination of the amount of CH consumed due to the hydration of the GP-CH and glass powder blended cement with time is also described in detail in Chapter 3 and Chapter 4.

Equation (4.23) represents the CH consumption rate due to the glass powder hydration in cement as a function of different parameters such as GP/C ratio, time, and activation temperature. Increasing the rate of CH loss due to the GP-CH hydration in cement indicates the reactivity of the glass powder.
5.2.2 Factors Affecting Reactivity

The reactivity of the glass powder is influenced by several factors, some of them are the inherent properties of the glass powder itself, and the others are environmental factors. Some of these factors are discussed in the following section.

5.2.2.1 Structure of the Glass Powder

It is important to properly define the term “glass”. The definition given by the American Society for Testing and Material is: “Glass is an inorganic product of fusion which has cooled to a rigid condition without crystallizing”. Particularly, the oxide glasses based on silica: the alkali-alkali earth-silica family of glasses are described.

The first theory of the structure of glass to become widely accepted was that of Zachariasen (1932), which is called the random network theory. This theory explains many characteristics of glassy states such as:

1- The optical isotropy of glasses results from the random atomic arrangement.

2- No two atoms occupy the same sites in the random network; hence, the lack of abrupt change of state can be understood.

3- The composition of glass is not stoichiometric (it is a mixture).

4- There are no crystal cleavage planes in glass.

Because of the random network theory, glass-forming oxide has been classified as a network former, network modifiers, and intermediates. Network formers are those found in the vitreous states as pure substances (SiO₂, GeO₂, B₂O₃...). The network modifiers disrupt the continuity of the network changing the chemical and physical properties and drop the working temperature. This category includes the alkali metal oxide (Na₂O, K₂O) and alkaline earth oxides (CaO, MgO). Intermediates are oxides, which can either enter the network as a network former or occupy interstitial holes as network modifiers, but are unable to form
glasses by themselves. Included in this class are alumina, titania and zirconia (Al₂O₃, TiO₂, ZrO₂) that play an important role in stabilizing the network.

In the archaeological glasses, the principal network former is silica (SiO₂) with the alkalis (soda Na₂O and potassia, K₂O) and alkaline earth (lime, CaO and magnesia, MgO) as the network modifiers. Figure 1 represents a schematic representation of the vitreous SiO₂ modified by Na₂O showing bridging and not bridging oxygen sites according to the random network theory.

The network forming elements are characterized by small ionic radii and by high possible ionic valences which are surrounded by four bridging oxygen atoms (BO) in the form of a tetrahedron. These bridging oxygen atoms connect the different tetrahedra with each other. The inclusion network modifiers break the bonded oxygen and form non-bridging oxygen atoms (NBO), O⁻, and free oxygen O²⁻. The typical network modifier within the glass structure is the Ca²⁺ ions. The polymerization grade of the network forming SiO₄⁺ tetrahedra is reduced with increasing the network modifier content, indicating that the glass has a smaller stability and higher chemical reactivity.

Figure (5.1): Schematic Representation of the Vitreous SiO₂ Modified by Na₂O Showing Bridging and Non-bridging Oxygen Sites According to the Random Network Theory
Clark and Zoitos (1992) correlated the calculated free energy of glass hydration for 150 different types of glasses with the number of non-bridging oxygen. The correlation gave a linear relationship between the free energy and the number of non-bridging oxygen for all the glasses used; where, the free energy decreases by increasing the NBO. Generally a lower free energy of hydration corresponds to lower stability and higher chemical reactivity of glass in the alkaline environment. Hence, the glasses with higher NBO values are more reactive than those with lower NBO values.

5.2.2.2 pH Value of the Pore Solution

Paul (1977) defined the reaction rate of glass as highly dependent on the chemical environment. After contacting with water, the reactivity of glass is mainly affected by the composition of the pore solution.

There are three major types of solutions: the acids (pH value below 5), the neutral (pH value between 5 - 9) and basic (pH value above 9) (Doremus, 1979). Normal glass is stable in a natural environment. However, in the cement hydration matrix, where pH value are above 9, glass starts to react and the breakdown of the glass silicate lattice is enhanced.

Reaction of Silicate Glass with Aqueous Solution

There are three different chemical reactions that can describe the corrosion of silicate glass when it is exposed to aqueous solutions (Paul, 1977).

1. The penetration of a proton from water into the glassy network, replacing an alkali ion.

\[ \equiv Si - OR + H_2O \rightarrow \equiv Si - OH + R^+ + OH^- \]  \hspace{1cm} \text{Eq. 5.1}

where, R is the alkali ion.

2. The hydroxyl ion in the solution disrupts siloxane bond in glass

\[ \equiv Si - O - Si \equiv +OH^- \rightarrow \equiv Si - OH + \equiv Si - O^- \]  \hspace{1cm} \text{Eq. 5.2}
3. The non-bridging oxygen formed in Eq.(5.2) interacts with a molecule of water to provide a hydroxyl ion.

\[ \equiv Si - O^- + H_2O \rightarrow \equiv Si - OH + OH^- \]

Eq. 5.3

According to the reaction in Eq.(5.1), the penetration of a base proton is energetically improbable as the hydration energy of H\(^+\) to H\(_3\)O is very high and negative. Therefore, the reaction Eqs.(5.2) and (5.3) dominate the dissolution of the silicate glass. The hydroxyl ion serves as the source of hydroxyl for further breaking of siloxane bond on the glass surface. Therefore, an increase in the activity of hydroxyl ion in the solution will activate the silica removal.

Paul (1977) calculated the solubility of the SiO\(_2\) using a thermodynamic approach and considering the effect of pH of the solution. It is concluded that the solubility of SiO\(_2\) is greatly enhanced when the pH goes above 9, as shown in Figure (5.2).

![Figure (5.2): Stability of SiO\(_2\) in Aqueous Solutions at Different pH, (Paul, 1977)](image)

This conclusion is also confirmed by the experimental results in chapter 3. According to Figure (3.20), the reactivity of the glass powder is affected by the pH. The hydration reaction starts at pH > 9.5, then the glass reactivity increases by increasing the pH of the solution.
5.2.2.3 Fineness of the Glass Powder Particles

Particle size of the glass plays an important role on its reactivity. By increasing the fineness of the glass powder particles, the reactivity is enhanced. According to the experimental results in Chapter 3, all the glass particles of sizes smaller than or equal to 2.5µm have totally reacted during the hydration period of 14 days at a temperature of 80°C. The bigger particles need more time and activation to react. The rate of hydration is actually proportional to the total surface area. Therefore, it is expected that fine glass powder particles hydrate much faster than the coarser ones.

5.2.2.4 Activating Temperature

The influence of the temperature on the glass powder reaction is very obvious. The glass powder reaction rate is even more sensitive than that of Portland cement systems. The activation energy $E_a$ of the glass powder can be calculated from the Arrhenius equation based on the hydration temperature $T$. The Arrhenius equation can be written in the form:

$$k_T = A \cdot \exp\left(\frac{-E_a}{RT}\right)$$  \hspace{1cm} \text{Eq. 5.4}

in which $k_T$ is the rate constant, $R$ is the gas constant (8.314x 10-3 kJ/(mol.K)) and $A$ is a constant.

5.3 Computer Modelling of Glass Powder Blended Cement Hydration

The CEMHYD3D computer model (Bentz, 1997, 2000, 2005) is modified to simulate the glass powder blended cement hydration to obtain a new model, which is called the “Mod-Model”. As mentioned earlier in Chapter 2, CEMHYD3D simulates the hydration process of Portland cement using a series of C-codes to simulate the hydration of cement components in a series of steps. The first step is to generate the cement particles in the computational volume according to its different particle sizes. Then, these particles are
sorted to the different cement components $C_3S$, $C_2S$, $C_3A$, and $C_4AF$. Then, the hydration of the cement components can start according to the selected hydration condition such as the activation temperature, ambient temperature, curing conditions, number of hydration cycles, etc. The model also simulates the hydration of some pozzolanic materials such as fly ash, silica fume and slag.

The simulation of glass powder hydration reactions in a cement matrix is merged in the CEMHYD3D model. The following sections represent the description of the glass powder hydration incorporation in the CEMHYD3D model to obtain the MOD-model in detail. Discussion of the MOD-model results and a comparison between the MOD-model and CEMHYD3D is also carried out.

### 5.3.1 Generating Glass Powder Pixels in the Computational Volume

The cement and glass powder particles are placed as spherical particles in the computational volume of $100 \times 100 \times 100$ pixels. Periodic boundaries are employed to prevent the particles from extending outward through one or more faces of the 3D microstructure. The particles of cement and glass powder are generated simultaneously in the order from largest to smallest. The generation of the particles is carried out in two steps. The particles of sizes of 3 pixels or more are generated first in the particle generation computer model inputs. Then the particles of small sizes of 1 pixel are generated in the hydration computer model inputs.

There are three different groups of pixels inside the computational volume before the hydration takes place. These groups are cement, glass powder and water. The number of pixels of the cement, glass powder and water in the computational volume can be calculated using Eqs. 5.5 to 5.7.

\[
V_c = \frac{1000000}{1.28X + 3.2Z + 3.2XZ + 1} \quad \text{Eq. 5.5}
\]

\[
V_{GP} = \frac{1.28X (1000000)}{1.28X + 3.2Z + 3.2XZ + 1} \quad \text{Eq. 5.6}
\]
\[ V_w = \frac{Z(3.2 + 3.2X)(1000000)}{1.28X + 3.2Z + 3.2XZ + 1} \]  
\text{Eq. 5.7}

Where, \( X = \frac{GP}{C}, \) \( Z = \frac{W}{S} \)

Also \( V_c, V_{GP} \) and \( V_w \) are the number of pixels of cement, glass powder and water respectively, \( X \) is the glass powder to cement ratio and \( Z \) is the water/solid ratio.

These Equations are based on the fact that the computational volume consists of one million pixels and the specific gravities of the cement and glass powder are 3.2 and 2.5 t/m³.

### 5.3.2 Incorporation of Glass Powder Hydration in CEMHYD3D

In the MOD-model, the hydration reaction of the glass powder has been incorporated into the hydration model of CEMHYD3D. The reaction model, Eq. 4.1, and its assumptions are used in the MOD-model. This model describes the hydration reaction of the glass powder with calcium hydroxide (pozzolanic type reaction) to produce a single (mixed phase) hydration product. This product would be a mixture of a C-S-H-type gel with Ca/Si ratio that is lower than the Ca/Si ratio of the conventional C-S-H-type gel.

A data file called “glasschar.dat”, which contains all the required data of the glass powder hydration characteristics, is created for the modelling and is used during the execution of the hydration model. The data includes specific gravity, molar volume and Ca/Si, H/Si molar ratios of the glass powder and its hydration product. The data was obtained experimentally in Chapters 3 and 4.

The hydration of the glass powder grains is executed in the hydration model as follows: the glass powder grains are basically hydrated in place. The glass powder voxels that are in contact with water-filled capillary porosity become eligible for conversion to a glass powder hydration product when it colligates with CH pixels produced from the hydration of the C₃S and C₂S pixels. The complete hydration of the clinker is assumed. In the real pastes of the glass powder blended cement, the clinker phases and the glass powder react simultaneously. These simultaneous reactions are represented in the computer model by the congruent
dissolution of the glass powder and clinker pixels. At each hydration cycle, the number of reacted clinker phases and glass powder can be counted. Therefore, the number of conventional C-S-H and glass powder C-S-H can be counted in each cycle.

The changes of alkalinity nature of the pore solution due to the alkaline release from the glass powder during the hydration are accounted for in the MOD-model execution. The data of the alkaline concentration in the pore solution, which is obtained experimentally in Chapter 4, is used in the data file called "alkalichar.dat". The data file is used during the execution of the hydration model.

The consumption of CH by the glass powder hydration is simulated by reducing the number of diffusing CH pixels to be added. The number of pixels to be reduced is calculated from Eq. 4.32 using the numbers of diffusing CH pixels generated by the clinker hydration and dissolved glass pixels. The remaining diffusing CH pixels are added randomly.

5.3.3 Relating Cycles to Real Time

Bentz (1997) proposed a method to relate the number of cycles executed in the simulation to the real time as in Eq. 5.8. Since the empirical relation is proven successful for Portland cement hydration, Bentz (1997), it is postulated and verified valid for glass powder blended cement hydration as well.

\[ t = B \times (cycles)^2 \]  

Eq. 5.8

in which \( t \) is the real time in (hours), \( B \) is the time conversion factor in (hour/cycle^2) of values ranged from \( 0.3 \times 10^{-3} \) to \( 1.7 \times 10^{-3} \) hour/cycle^2, \( (cycles) \) are the number of executed calculations or model cycles.

5.3.4 Required Data for Simulations

For simulating the hydration of glass powder blended cement, the following information is needed:
• The composition and PSD of clinker and gypsum (if present),

• The PSD of the glass powder,

• Glass powder/cement ratio,

• Water/binder ratio, and

• Curing condition, including the temperature and sealed/saturated state.

The hydration is carried out on a cycle basis and then converted into time.

Also required is some information about the glass powder and the glass powder hydration product GP C-S-H. The data file “glasschar.dat” includes all the physical and chemical characteristics of the glass powder hydration including the:

• Molar mass of the glass powder (gm/mole).

• Molar mass of the glass powder hydration product, GP C-S-H, (gm/mole).

• Specific gravity of the glass powder.

• Specific gravity of the glass powder hydration product, GP C-S-H.

• Molar volume of the glass powder.

• Molar volume of the glass powder hydration product, GP C-S-H.

• Ca/Si molar ratio of the glass powder.

• Ca/Si molar ratio of the glass powder hydration product, GP C-S-H.

• Si atoms number per molar unit of glass powder

• $\text{H}_2\text{O}/\text{Si}$ molar ratio in the glass powder hydration product, GP C-S-H.

The specific gravity of the glass powder hydration product, GP C-S-H, gel is assumed as approximated value as slag hydration product $= 2 \text{ gm/m}^3$. For simulating the amount of alkalis released in the pore solution due to the hydration with time, the data file “alkalichar.dat” is created and includes the following information:

• Sodium oxide content of the glass powder blended cement being modeled,

• Potassium oxide content of the glass powder blended cement being modeled,

• Readily-soluble (1h) sodium oxide content of the glass powder blended cement,
• Readily-soluble (1h) potassium oxide content of the glass powder blended cement.

The data required for the simulation was obtained experimentally, in Chapters 3 and 4, based on one type of glass powder with a certain particle size distribution. After each hydration cycle, properties evolving during the hydration process such as chemical shrinkage, heat release, non-evaporable water and porosity, are calculated using the inherent properties of the reaction and physical or chemical properties of the products.

5.4 Discussion

The MOD-model is examined to determine the differences of the physical and chemical properties between plain cement and glass powder blended cement pastes due to the incorporation of glass powder hydration with cement hydration modelling in the CEMHYD3D model. Different hydration simulation runs (implementations) are carried out for different glass powder blended cement pastes with different GP/C ratios of 0, 5, 10, 15, 20, 25, 30% used with ordinary Portland cement (Type 10). All the tested pastes have a water/solid ratio of 0.5 and are tested under the same conditions. Curing in a sealed condition, ambient temperature of 25°C and 3000 cycles of hydration with time conversion factor equal to $3.5 \times 10^{-3}$ hour/cycle² are used in the simulation execution. The particle sizes of the cement and glass powder used for the simulation generation are taken as the material data used in the experiments detailed in Chapters 3 and 4.

The phase development of the hydration products and the disappearance of glass powder due to hydration for three different pastes of GP/C ratios 0, 10, 20% are plotted in Figures (5.3 to 5.5) as volume fractions. As shown in the figures, the glass powder disappearance is very slow and increases in the pastes of the higher GP/C ratios. The CH content decreases in the pastes of the higher GP/C ratios. The conventional C-S-H content is almost the same for all the pastes; however, the glass powder C-S-H content increases by an increase in the glass powder content in the paste.
The following sections include discussions about the degree of hydration, CH content in the paste, C-S-H content, pH development, alkalis in the pore solution and the microstructure development of the different simulated pastes. A comparison between the characteristics of the plain pastes of (GP/C) ratio = 0%, which are obtained from CEMHYD3D model and those of the glass powder blended cement pasted, which are obtained from MOD-model, is carried out to clarify the differences between the two models.

Figure (5.3): The Phase Development of the Hydration Products for the Hydrated Paste of GP/C ratio = 0% Obtained by MOD-Model
Figure (5.4): The Phase Development of the Hydration Products for the Hydrated Paste of GP/C ratio = 10% Obtained by MOD-Model

Figure (5.5): The Phase Development of the Hydration Products for the Hydrated Paste of GP/C ratio = 20% Obtained by MOD-Model
5.4.1 Degree of Hydration of Glass Powder Blended Cement

The D.O.H development with time for the different pastes is plotted in Figure (5.6). As shown in the figure, the D.O.H development along a period of more than 3000 hours of hydration is affected by the glass powder addition in the pastes so that the D.O.H values of the glass powder pastes are greater than those in the plain paste. However, there are no noticeable differences in the D.O.H values with time among the glass powder pastes when altering the glass powder additions. The behaviour of the D.O.H development of the different pastes can be explained by the fact that the reactivity of the glass powder can increase the overall hydration degree of the pastes. It is noticed that the glass powder addition can increase the D.O.H of the pastes by about 30% more than the D.O.H of the plain pastes.

5.4.2 CH Content in the Paste

The CH content development with time for the different pastes is plotted in Figure (5.7) as a fraction of the total volume. The figure shows the CH content development for the pastes of different GP/C ratios that range from 0 to 30% along more than 3000 hours of hydration. Generally, the CH content is increased with time for all the pastes due to the continuation of the hydration. However, the rate of increase declines for the pastes of higher glass powder content due to the consumption of CH in the glass powder hydration. The total consumption of CH content due to the glass powder hydration in the paste of GP/C ratio of 30% is about 23% of the total CH content produced from the cement hydration in the plain paste.

5.4.3 Content of C-S-H

5.4.3.1 Conventional C-S-H

The C-S-H produced by the cement hydration for the different pastes with time is plotted in Figure (5.8) as a fraction of the total volume. It is noted that the C-S-H content increases with time for the different pastes of different glass powder content. However, this increase slightly declines by increasing the glass powder content in the pastes. This behaviour occurs
because the total amount of cement in the hydration computational volume is decreased by increasing the glass powder amount in the same computational volume. Hence, the C-S-H produced from the cement hydration decreases as well.

### 5.4.3.2 Glass Powder C-S-H

For the different glass powder pastes, the GP C-S-H content increases with an increase of glass powder content in the paste, as shown in Figure (5.9). It is noted that the total increase of the GP C-S-H content in the paste of GP/C ratio of 30% is about 6 times that for the paste of GP/C ratio of 5%. The overall amount of C-S-H content produced in the pastes (conventional and GP C-S-H) with time is plotted in Figure (5.10) as a fraction of the total volume. It is shown that the total C-S-H content increases with time and with an increase of glass powder content in the paste.

![Graph showing D.O.H development versus time for different pastes](image)

**Figure (5.6): The D.O.H Development versus Time for the Different Pastes Obtained by the MOD-Model**
Figure (5.7): The CH Content Development versus Time for the Different Pastes Obtained by the MOD-Model

Figure (5.8): The C-S-H Content Development versus Time for the Different Pastes Obtained by the MOD-Model
Figure (5.9): The GP C-S-H Content Development versus Time for the Different Pastes Obtained by the MOD-Model

Figure (5.10): The Total C-S-H Content Development versus Time for the Different Pastes Obtained by the MOD-Model
5.4.4 pH Development

Due to the highly alkaline nature of glass powder pastes, there are significant differences in the pH values between the plain and glass powder pastes, as shown in Figure (5.11). It is shown that for all the pastes, the maximum value of the pH is obtained after a small period of hydration, and then this value remains constant along the hydration period. The pH values increase with an increase of the glass powder content in the paste. The pH values change from 13.5 to 14 for the pastes of GP/C ratio increasing from 5 to 30%.

5.4.5 Na Concentration in the Pore Solution

The concentrations of the Na ions in the pore solution for the different pastes have been determined experimentally in Chapter 4. These experimental results are used in the MOD-model simulation in the “alkalichar.dat” data file, which contains the total released sodium content from the glass powder cement hydration during the hydration period. The concentration of the Na ions in the pore solution during more than 3000 hours of hydration for all the pastes is plotted in Figure (5.12) as a weight percentage. It is shown that the Na concentration in the pore solution increases with an increase in the glass powder content in the pastes. In the plain paste, the maximum amount of Na ions in the pore solution along the hydration period is 0.2%. However, the maximum amount of Na ions in the pore solution for the glass powder blended cement pastes increases from 1 to 2.2% for the pastes of GP/C ratio equal to 5 and 30% along 3000 hours of hydration. This increase in the pore solution alkalinity is resulted from the high concentration of Na ions in the glass powder structure, which are released during the glass powder hydration and increase due to the glass powder content in the paste.
Figure (5.11): The pH Development versus Time for the Different Pastes Obtained by the MOD-Model

5.4.6 Microstructure Development

Figures (5.13 to 5.16) illustrate the 3D images of the microstructure of the pastes of GP/C ratios of 0, 10, 20 and 30% after a period of 3000 hours of hydration at a temperature of 25°C. It focuses on the pixels distribution of the porosity, CH, C-S-H, GP C-S-H and the glass powder in these images. These components are the most important for the glass powder blended cement simulation.
Figure (5.12): The Na Concentration Development versus Time for the Different Pastes Obtained by the MOD-Model

The first image illustrates the microstructure distribution of the different cement hydration components. The main components here are the C-S-H in green, CH in yellow and the porosity in cyan. It is shown that these components are in a good propagation inside the computational volume, yet noticing that the C-S-H content is higher than the CH content.

Figures (5.14 to 5.16) illustrate the microstructure distribution of the different glass powder blended cement hydration components of GP/C ratio = 10, 20 and 30%, respectively. The main components here are the C-S-H in green, CH in yellow, GP in red, GP C-S-H in dark-red and the porosity in cyan. In Figure (5.14), new colours start to appear in the computational volume besides the main colours of the C-S-H, CH and the porosity. These colours are the red and the dark-red colours expressing the existence of GP and GP C-S-H pixels. These new colours appeared due to the existence of the hydration of the glass powder in the computational volume according to the MOD-model. As shown in the figure, The GP pixels are placed in a scattered manner surrounded by the GP C-S-H pixels. This is because when the glass powder pixels, which are in contact with water pixels, collide with the CH pixels, the glass powder pixels convert to GP C-S-H pixels in place covering the GP surface. Also, it is noticed that the CH content decreases in the computational volume due to the glass powder hydration. By increasing the glass powder content in the computational volume, as
shown in Figures (5.15 and 5.16), the content of the GP and GP C-S-H increase. It is noticed in Figures (5.15 and 5.16) that the small particles of GP are totally converted to GP C-S-H and the amount of CH declines. It is also noticed that the C-S-H and the porosity contents decrease slightly by increasing the GP content.

5.5 Conclusions

In this chapter, the MOD-model has been developed for simulating the hydration and microstructure development of glass powder blended cement pastes. The theoretical models developed in Chapters 3 and 4 were used and incorporated into the computer model. Various factors that affect the glass powder reactivity are discussed. The required data for the modelling is also included. Discussions of the modelling results due to the glass-powder hydration incorporation in the computer model are shown. In addition, a comparison between the MOD-model and CEMHYD3D model results are made.

It is concluded from the MOD-model results that the glass powder hydration inside the cement hydration matrix affects the overall D.O.H, CH content, C-S-H content, pH and pore solution alkalinity of the tested pastes. The D.O.H is affected by the glass powder addition in the pastes so that the D.O.H values of the glass powder pastes are greater than those in the plain paste. The total consumption of the CH content due to glass powder hydration in the paste of GP/C ratio of 30% is about 50% of the total CH content produced from the cement hydration in the plain paste. A new hydration product that appears due to the hydration of the glass powder, which is referred to as GP C-S-P, increases with an increase in the glass powder content in the paste. The total C-S-H content, which includes the conventional C-S-H and the GP C-S-H, increases with time and with an increase of the glass powder content in the paste. Moreover, the pH values increase with an increase of the glass powder content in the paste. The pH values change from 13.5 to 14 for the pastes of GP/C ratio increasing from 5 to 30%. The Na concentration in the pore solution increases with an increase in the glass powder content in the pastes. The hydrated paste microstructure is affected by the glass powder addition in the pastes so that the GP and the GP C-S-H pixels increase in the computational volume with an increase of the glass powder content in the paste.
Figure (5.13): Three-Dimensional Central Image from the Final 3-D Microstructure for Pastes of GP/C Ratio of 0% and for w/c=0.50. Colour Assignments are Cyan- Porosity, Green- C-S-H, Yellow- CH, Red- GP, and Dark Red- GP C-S-H

Figure (5.14): Three-Dimensional Central Image from the Final 3-D Microstructure for Pastes of GP/C Ratio of 10% and for w/c=0.50. Colour Assignments are Cyan- Porosity, Green- C-S-H, Yellow- CH, Red- GP, and Dark Red- GP C-S-H
Figure (5.15): Three-Dimensional Central Image from the Final 3-D Microstructure for Pastes of GP/C Ratio of 20% and for w/c=0.50. Colour Assignments are Cyan- Porosity, Green- C-S-H, Yellow- CH, Red- GP, and Dark Red- GP C-S-H

Figure (5.16): Three-Dimensional Central Image from the Final 3-D Microstructure for Pastes of GP/C Ratio of 30% and for w/c=0.50. Colour Assignments are Cyan- Porosity, Green- C-S-H, Yellow- CH, Red- GP, and Dark Red- GP C-S-H
CHAPTER 6

VERIFICATION OF THE DEVELOPED GLASS POWDER BLENDED CEMENT COMPUTER MODEL

6.1 Introduction

In Chapter 5, a new model, which is referred to as the MOD-model, was proposed to theoretically simulate the hydration behaviour of glass powder blended cement based on the CEMHYD3D model. To validate this model, comparisons between the experimental results, obtained in Chapter 4, and the theoretical results, obtained from the MOD-model outputs, of glass powder blended cement hydration properties are made in this chapter. Different runs of the MOD-model for different glass powder additions are executed using the same parameters used in the experimental work such as GP/C ratio, w/s ratio, activation temperatures, and curing conditions. Comparisons between the D.O.H, Na concentration in the pore solution and CH consumption obtained experimentally in Chapter 4 and those, which are obtained theoretically from MOD-model, are made to validate the computer model. Comparisons for the chemical shrinkage are also made and presented in this chapter.
6.2 Model Parameters

Two different groups of experiments are carried out. In the first group (Group I in Table 6.1) D.O.H, Na concentration in the pore solution and CH consumption are determined. In the second group (Group II), the chemical shrinkage is determined. Each group is carried out using different parameters and hydration conditions. Two groups of runs are executed using the computer MOD-model considering different parameters and hydration conditions used in the experimental work. Table (6.1) summarises the different parameters used in the computer model. The particle size distribution of the cement and glass powder used in the experimental work are considered in the execution of the computer model.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Group (I)</th>
<th>Group (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP/C Ratio (%)</td>
<td>0, 5, 10, 15, 20, 25, and 30</td>
<td>0, 10, and 20</td>
</tr>
<tr>
<td>w/s Ratio</td>
<td>0.5</td>
<td>0.4, 0.5 and 0.6</td>
</tr>
<tr>
<td>Hydration Temperature</td>
<td>25, 40, and 80°C</td>
<td>25°C</td>
</tr>
<tr>
<td>Curing Conditions</td>
<td>Sealed</td>
<td>Sealed</td>
</tr>
<tr>
<td>$\beta$ Conversion Factor</td>
<td>$3.5 \times 10^{-3}$ hour/cycles$^2$</td>
<td>$3.5 \times 10^{-3}$ hour/cycles$^2$</td>
</tr>
</tbody>
</table>

6.3 MOD-Model Validation

In the following sections, the experimental results of the D.O.H, Na concentration in the pore solution, CH consumption due to the GP hydration in the cement matrix, which are determined in Chapter 4 using GP/C ratios equal to 0, 5, 10, 15, 20, 25, and 30%, w/s ratio of 0.5 and hydration temperatures 25, 40, and 80°C, are used to evaluate the results obtained from the computer model. Chemical shrinkage tests for different glass powder blended cement pastes of GP/C ratios equal to 0, 10, and 20%, w/s ratios of 0.4, 0.5, and 0.6 hydrated at temperature of 25°C is carried out to verify the chemical shrinkage results obtained from the model.
6.3.1 Degree of Hydration

Figures (6.1 to 6.3) show the relationships between the D.O.H results obtained experimentally and theoretically with time for all the glass powder blended cement pastes hydrated at temperatures of 25, 40 and 80°C. It can be seen that the model results of the plain cement paste hydrated at 25°C, give values lower than those obtained experimentally. That is because the sealed curing condition, which is used in the modelling, can result in a re-percolation of the capillary porosity that was initially de-percolated by the hydration of the cement. The re-percolation of the capillary porosity may delay the continuation of the hydration and decrease the degree of the hydration (Bentz, 2006). However, for the glass-powder cement pastes, there is a good agreement between the experimental and theoretical results. This is because of the existence of the glass powder particles in the model computational volume beside the porosity and cement. The glass powder particles can impede the re-percolation of the capillary porosity that is caused by the sealed curing condition which affects the degree of hydration. Hence, the degree of hydration of the glass powder cement pastes is slightly affected by the sealed curing condition. The agreement between the experimental and theoretical result increases for the pastes hydrated at temperatures of 40 and 80°C. For the pastes hydrated at 25°C, it is noticed that for the first 72 hours of hydration, the D.O.H obtained theoretically are lower than those obtained experimentally. By increasing the hydration temperature, the difference between the theoretical and the experimental results at the early age is narrowed. For later ages, the differences between the theoretical and the experimental results are further narrowed specially by increasing the activation temperature.

6.3.2 Alkalis in the Pore Solution

The experimental and theoretical results of the Na concentration in the pore solution for all pastes hydrated at temperatures 25, 40 and 80°C are plotted in Figures (6.4 to 6.6). As a result of the release of Na in the pore solution from the glass powder structure during the hydration, the concentration of the Na in the pore solution of the glass powder cement paste of GP/C ratio = 30% increases 10 times that in the plain cement pastes in the later ages. The experimental values are in reasonable agreement with the theoretical values especially at early ages, which can be seen in Figures (6.5 and 6.6). With time, the differences between the
Theoretical and the experimental results are narrowed specially when increasing the activation temperature from 25 to 80°C. The best agreement between the theoretical and experimental results can be noticed in the pastes that hydrated at 80°C. Also, it is noticed that in all curves there are some discrepancies between the experimental and theoretical results for the pastes of higher GP/C ratios, e.g., 25 and 30%. However, in general, there is a good agreement between the experimental and the model results for the Na concentration in the pore solution.

Figure (6.1): Relationships between the Experimental and Theoretical D.O.H Results and the Time for All the Pastes Hydrated at Temperatures of 25°C
Figure (6.2): Relationships between the Experimental and Theoretical D.O.H Results and the Time for All the Pastes Hydrated at Temperatures of 40°C
Figure (6.3): Relationships between the Experimental and Theoretical D.O.H Results and the Time for All the Pastes Hydrated at Temperatures of 80°C
Figure (6.4): Relationships between the Experimental and Theoretical Na Concentration in the Pore Solution Results and the Time for All the Pastes Hydrated at Temperatures of 25°C
Figure (6.5): Relationships between the Experimental and Theoretical Na Concentration in the Pore Solution Results and the Time for All the Pastes Hydrated at Temperatures of 40°C
Figure (6.6): Relationships between the Experimental and Theoretical Na Concentration in the Pore Solution Results and the Time for All the Pastes Hydrated at Temperatures of 80°C
6.3.3 CH Consumption

The CH consumption values as a percentage are calculated by dividing the difference between the CH content in the plain cement paste and that in the glass powder cement pastes over the CH content in the plain cement paste. The CH content in the glass powder cement pastes is lower than that in the plain cement paste. It decreases with an increase in the glass powder proportions in the cement.

Figures (6.7 to 6.9) show the relationships between the CH consumption with time for all the glass powder cement pastes hydrated at temperatures 25, 40 and 80°C. The model values of the CH consumption are also plotted in the same figures. It can be seen that the CH consumption values increase with an increase in the glass powder proportions in the cement. These values increase rapidly at the early ages followed by approximately constant values at later ages. The trend of the increase and the values of the model results are in good agreement with the experimental measurements. As shown in Figures (6.7 and 6.8), which represent the experimental and theoretical results of the pastes activated at temperatures of 25 and 40°C, respectively, there are good agreements between the experimental and theoretical results for the pastes of GP/C ratios, e.g., 0 to 30%. For the pastes, which are activated at 80°C, as shown in Figure (6.9), there are some discrepancies between the experimental and the predicted results in the earlier age. By increasing the time, the differences between the experimental and the theoretical results decrease.
Figure (6.7): Relationships between the Experimental and Theoretical CH Consumption Results and the Time for All the Pastes Hydrated at Temperatures of 25°C
Figure (6.8): Relationships between the Experimental and Theoretical CH Consumption Results and the Time for All the Pastes Hydrated at Temperatures of 40°C
Figure (6.9): Relationships between the Experimental and Theoretical CH Consumption Results and the Time for All the Pastes Hydrated at Temperatures of 80°C
6.3.4 Chemical Shrinkage

Figures (6.10 to 6.12) show the relationship between the chemical shrinkage values obtained experimentally and theoretically and the time for the pastes of w/s ratios of 0.4, 0.5, and 0.6. The chemical shrinkage values increase rapidly at the early ages followed by approximately constant values at the later ages. As shown in Figure (6.15), which represents the experimental and the theoretical results of the pastes hydrated of w/s ratios of 0.4, 0.5 and 0.6, there are discrepancies between the experimental and the predicted results in the early ages. With time, the differences between the experimental and the theoretical results decline. This can be explained as before in the D.O.H validation, where the sealed curing conditions used in the model may delay the hydration of the pastes. This delay affects the chemical shrinkage of the pastes to be decreased. However, in general there is reasonable agreement between the experimental and the predicted results.

![Figure (6.10): Relationships between the Experimental and Theoretical Chemical Shrinkage Results and the Time for All the Pastes of w/s=0.4](image-url)
Figure (6.11): Relationships between the Experimental and Theoretical Chemical Shrinkage Results and the Time for All the Pastes of w/s=0.5

Figure (6.12): Relationships between the Experimental and Theoretical Chemical Shrinkage Results and the Time for All the Pastes of w/s=0.6
6.4 Conclusions

In this chapter, the model predictions have been validated with measurements of experiments reported in Chapter 4. The model has been further used to investigate a few properties of hydrating glass powder cement paste. These properties are the D.O.H of the paste, the Na concentration in the pore solution, CH consumption by the glass powder hydration and the chemical shrinkage of the pastes. For the pastes hydrated at 25°C, it is noticed that for the first 72 hours of hydration, the D.O.H obtained theoretically are lower than those obtained experimentally. By increasing the hydration temperature, the difference between the theoretical and the experimental results in the early age is narrowed. For the Na concentration results, the differences between the theoretical and the experimental results are narrowed specially when increasing the activation temperature from 25 to 80°C. The best agreement between the theoretical and experimental results can be noticed in the pastes that hydrated at 80°C. For the CH consumption values, there is a good agreement between the experimental and theoretical results for the pastes of lower GP/C ratios of 0 to 20%. By increasing the GP/C ratio to 25% and 30%, discrepancies between the experimental and the predicted results appear. There are also good agreements between the experimental and the predicted chemical shrinkage results for the glass powder blended cement pastes. In general, all the results show that the MOD-model is able to simulate the hydration process of glass powder cement pastes and can be used to predict various properties of the hydrating paste.
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Introduction

The use of glass waste in the concrete industry is new and attracts many interests. There is a clear lack of research works that have studied glass powder blended cement behaviour. The existing researches have investigated the behaviour of the concrete using different types of glass powder as a partial replacement of cement and aggregates. The particle size of the glass powder determines whether it is used as a partial replacement of cement (fine particles) or aggregates (course particles). The application of glass powder cement in concrete is still in its infancy. Research at this stage is focusing on investigating the effect of the glass powder addition on the properties of the concrete. These properties include the compressive strength of concrete, durability, aggregate silica reaction and permeability.

The study of glass powder cement hydration on the microstructure level is also relatively new. To the author's knowledge, investigating the hydration reaction of glass powder in activated and cement media has not been tackled before. In this thesis, the hydration characteristics of activated glass powder and glass powder blended cement are studied. Theoretical models that describe the hydration reaction of the glass powder in the activated and cement media are proposed. Experimental programs are also carried out to investigate the hydration properties of the glass powder in the activated and cement media (Chapters 3
and 4). Information about the glass powder such as the glass content, oxide composition, particle size distribution (PSD), etc. is important to study the hydration of the glass powder blended cement. The CEMHYD3D model developed by Bentz (2000, 2005) has been chosen for modelling the hydration of glass powder blended cement, which has been developed for over 10 years (Chapter 2). A new computer model referred to as the MOD-model, which incorporates glass powder hydration in the CEMHYD3D computer model and simulates the hydration of glass powder blended cement is developed. Chapter 5 contains the computer modelling details, the inputs and outputs of the MOD-model. The differences between the MOD-model and CEMHYD3D model results are also discussed in Chapter 5. Chapter 6 contains comparisons between the experimental and the theoretical results of the glass powder blended cement characteristics.

The main conclusions of this research are summarized below.

7.2 Theoretical and Experimental Work for the Glass Powder Activated Hydration

Stoichiometric models describe the hydration of pure glass powder. Also, the hydration of the GP-CH reaction is established based on some assumptions of the glass powder oxides composition and the expected hydration products. It is assumed that the main and only hydration product is GP C-S-H. Experimental testing has been carried out to investigate the exact quantities of glass powder, CH and water, which enter the hydration reaction. Other experiments were also carried out to investigate the chemical and physical characteristics of the GP-CH hydration.

It is concluded that the D.O.H of the specimens increases with an increase of the CH/GP ratio. For the same CH/GP ratio, the pH of the specimens increases with time and with an increase in the activated temperature. The consumption rate of the CH due to the reaction decreases when increasing the CH/GP ratio. The optimum consumption of the CH is obtained in the specimen of CH/GP ratio of 20%. Finely ground glass powders exhibited very high pozzolanic activity. The finer the glass powder is, the higher is its pozzolanic activity. According to the SEM images taken for the microstructure of the GP-CH
specimens, it is concluded that the gel formation of the GP C-S-H fills the voids of the un-reacted big particle of the GP instead of the nano and very small micro particles in the same place before the hydration. This indicates that all of these small particles have reacted and converted to GP C-S-H gel formation.

Two different chemical formulas for the produced GP C-S-H gel due to the pure GP and GP-CH hydration are proposed. For the pure GP hydration, the produced GP C-S-H gel has a C/S ratio of 0.164, H/S ratio of 1.3 and N/S ratio of 0.18. However, for the pure GP-CH hydration, the produced GP C-S-H gel has a C/S ratio of 1.17, H/S ratio of 2.5 and N/S ratio of 0.18.

7.3 Theoretical and Experimental Work for Glass Powder Cement Hydration

A few theoretical models are available for the hydration of Portland cement and its microstructure development (Jennings and Tennis, 1994; Powers and Brownyard, 1948). The most well-known model is probably the Powers and Brownyard (1948) model, which calculates the volume fractions of phases in a hydrating Portland cement paste and other related properties such as the water binding and the chemical shrinkage. These theoretical models have been proven valuable for understanding the microstructure of hydrating Portland cement paste.

Stoichiometric models that describe the hydration reaction of the glass powder inside the cement matrix are established based on assumptions related to the glass powder and cement natures. A theoretical model is proposed to investigate the pore solution composition of hydrating glass powder blended cement paste. The methods by Taylor (1987b) and Brouwers and Eijk (2003) for alkali concentrations are considered. Methods for determining the alkali binding capacity of the C-S-H are proposed. The same methods are applied for hydrating the glass powder cement; i.e., the concept of alkali release and binding is applied.

Experiments were carried out to investigate the chemical and physical characteristics of the GP blended cement hydration. The consumption of the CH in the glass powder hydration
during the hydration period was also determined based on the experimental results. According to the experimental testing, it is concluded that pH of the glass powder cement pastes increases with an increase of the GP/C addition ratio with time. The consumption rate of the CH increases with time and with an increase in the activated temperature. The consumption rate of the CH due to the GP hydration increases when increasing the GP/C ratio. The maximum consumption of the CH due the reaction with the GP is about 50% of total amount of CH produced due to the cement hydration. The Na concentration in the pore solution increases 3 times when increasing the GP/C ratio from 0% to 30%. It is concluded from the SEM images that the C-S-H gel formation in the GP blended cement paste is denser and more coherent than that in the plain pastes. Also, the model that describes the CH consumption due to the GP hydration in the cement hydration matrix agrees reasonably well with the experimental results.

7.4 3-D Computer Modelling of Glass Powder Cement Hydration

One of the main objectives of this research was to simulate the glass powder blended cement hydration. A new computer model referred to as the MOD-model was developed to simulate the hydration of the glass powder blended cement. Different runs (implementations) of the MOD-model for different glass powder additions were executed to assess the model. The data needed to execute each run were collected from the experimental results as described in detail in Chapters 3 and 4.

According to the MOD-model results, it is concluded that the glass powder hydration inside the cement hydration matrix affects the overall D.O.H, CH content, C-S-H content, pH and pore solution alkalinity of the tested pastes. The D.O.H is affected by the glass powder addition in the pastes so that the D.O.H values of the glass powder pastes are greater than those in the plain paste. The total consumption of CH content as a result of the glass powder hydration in the paste of GP/C ratio of 30% is about 50% of the total CH content produced from the cement hydration in the plain paste. A new hydration product appears as a result of the hydration of the glass powder, which is called GP C-S-H. This product's
content increases with an increase in the glass powder content in the paste. The total C-S-H content, which includes the conventional C-S-H and the GP C-S-H, increases with time and with an increase of the glass powder content in the paste. The pH values increase with an increase in the glass powder content in the paste. The pH values change from 13.5 to 14 for the pastes of GP/C ratio increasing from 5 to 30%. The Na concentration in the pore solution increases with an increase in the glass powder content in the pastes. The hydrated paste microstructure is affected by the glass powder addition in the pastes so that the GP and the GP C-S-H pixels increase in the computational volume with an increase of the glass powder content in the paste.

The MOD-model predictions have been validated using the experimental results, and were further used to investigate various properties of the hydrated glass powder cement paste. These properties include, for example, the CH content in the paste, porosity, hydration degree of the glass powder and the content of the conventional C-S-H and GP C-S-H. The results show that the MOD-model is reasonably able to simulate the hydration process of glass powder blended cement and can be used to predict various properties of the hydrating paste.

7.5 Recommendations and Future Research

The experimental tests which were carried out in this research work describe the hydration characteristics of the activated glass powder and glass powder blended cement using one type of waste glass of a certain PSD and one type of cement. Only few properties relevant to the glass powder cement pastes have been examined in this thesis. Additional tests are necessary to cover all the properties of glass powder cement pastes using different types of waste glass of different PSD with different types of cement.

In this section, some recommendations are given based on the obtained experimental and theoretical results. Here, recommendations for possible future research are also presented.

- According to the experimental testing, which were carried out on glass powder blended cement mixes using Portland cement type, glass powder of maximum
particle size of 100μm and w/s = 0.5, it is recommended to use GP/C = 10% as an optimum ratio to achieve the best hydration and best properties of the paste.

• From the experiments, it is proven that glass powder has a pozzolanic effect on the glass powder cement pastes. Hence it is recommended to carry out more experiments for the glass powder blended cement using different types of cement and different types of the waste glass with different w/s ratios.

• The PSD and the maximum particle size of the glass powder have great effects on the hydration of the glass powder blended cement mixes. Hence it is recommended to carry out more experiments to examine the effect of using different glass powder patches with different PSD and the effect of the maximum particle size on the cement pastes.

• Further experiments are required to investigate the effect of using the glass powder cement with different GP/C ratios on the mechanical properties of the normal and high strength concrete.

• It is required to examine the GP C-S-H, which is produced from the glass powder cement hydration, in its nano-structure level to determine the differences between the conventional C-S-H and GP C-S-H.

• It is recommended to investigate the differences between the pozzolanic effect of the different pozzolanic materials such as fly ash, slag and silica fume and that of the glass powder on the concrete properties.

• Restrictions of the MOD-model apply as a result of the limited experimental work within the objectives of this research. More experiments on the glass powder blended cement are needed to further validate the model and to improve its reliability.
REFERENCES


