Fall 2007

Properties of alkaline-resistant calcium-iron-phosphate glasses

Jiawanjun Shi

Follow this and additional works at: http://scholarsmine.mst.edu/masters_theses

Department: Materials Science and Engineering

Recommended Citation
PROPERTIES OF ALKALINE-RESISTANT
CALCIUM-IRON-PHOSPHATE GLASSES

by

JIAWANJUN SHI

A THESIS

Presented to the Faculty of the Graduate School of the
UNIVERSITY OF MISSOURI-ROLLA
In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN CERAMIC ENGINEERING

2007

Approved by

Richard K. Brow, Advisor                     Delbert E. Day

Matthew J. O'Keefe
The physical properties and alkaline corrosion resistant properties of calcium-iron-phosphate glasses were studied. The addition of Fe$_2$O$_3$ decreases the thermal expansion coefficient and increases the glass fiber’s Young’s modulus in comparison with the addition of CaO. Bulk glass dissolution behavior in alkaline Lawrence solution was studied by weight loss experiments, Raman spectroscopy, and analytical scanning electron microscopy. The corrosion of glass powder in NaOH solution was studied by X-ray diffraction, infrared spectroscopy and high pressure liquid chromatography. The results show that the dissolution rate decreases when the phosphate chain length decreases. Calcium oxide can improve the glass durability in high pH solutions in comparison with ferric oxide. Phase equilibrium modeling was used to explain the formation of corrosion products, including hydroxyl apatite and Fe$_2$O$_3$. 
ACKNOWLEDGMENTS

My deepest thanks go to my advisor, Dr. Richard K. Brow, for all the guidance and inspiration he has given me throughout the research. From him, I learned the important elements to do research: to be strict at every detail and to treat every one nicely and honestly. I really feel happy and lucky to work in Dr Brow’s group for two and half years. His wisdom and experience have had a profound impact on my view of glass science and engineering.

I wish to thank my advisory committee members, Dr. Delbert E. Day, and Dr. Matthew J. O'Keefe for their time and expert guidance.

I do appreciate the support and love from my family, my mother Xiaoxia, my spouse Hao Zhang and my beloved angel Acacia.

I also had great help from Signo T. Reis, Eric Bohannan, Clarissa Vierrether, and all the members of my research group.

I would like to gratefully acknowledge the Department of Energy (Award Number DE-FC36-04G0 14046), the University Transportation Center, and MoSci, Inc., for their financial support.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1. CORROSION STUDIES OF CEMENT REINFORCEMENT GLASS FIBERS</td>
<td>1</td>
</tr>
<tr>
<td>1.2. PHOSPHATE GLASS STRUCTURE AND PROPERTIES</td>
<td>3</td>
</tr>
<tr>
<td>1.2.1. Glass Forming and Fiber Pulling Ability</td>
<td>3</td>
</tr>
<tr>
<td>1.2.2. Phosphate Glass Structure</td>
<td>3</td>
</tr>
<tr>
<td>1.2.3. Composition Effects on Glass Structure</td>
<td>5</td>
</tr>
<tr>
<td>1.2.4. Corrosion Study of Phosphate Glass</td>
<td>7</td>
</tr>
<tr>
<td>1.3. SUMMARY AND THESIS STATEMENT</td>
<td>10</td>
</tr>
<tr>
<td>2. EXPERIMENT PROCEDURES</td>
<td>11</td>
</tr>
<tr>
<td>2.1. SAMPLE PREPARATION</td>
<td>11</td>
</tr>
<tr>
<td>2.2. PHYSICAL PROPERTIES CHARACTERIZATION</td>
<td>13</td>
</tr>
<tr>
<td>2.3. CHEMICAL DURABILITY TESTS</td>
<td>13</td>
</tr>
<tr>
<td>2.4. SAMPLE CHARACTERIZATION</td>
<td>14</td>
</tr>
<tr>
<td>3. RESULTS</td>
<td>16</td>
</tr>
<tr>
<td>3.1. GLASS AND FIBER FORMATION</td>
<td>16</td>
</tr>
<tr>
<td>3.2. PHYSICAL PROPERTIES</td>
<td>17</td>
</tr>
<tr>
<td>3.3. CORROSION BEHAVIOR</td>
<td>20</td>
</tr>
</tbody>
</table>
## LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Composition of Calcium Iron Phosphate Glasses [16]</td>
<td>4</td>
</tr>
<tr>
<td>1.2</td>
<td>Phosphate Tetrahedral Sites that can Exists in Phosphate Glasses</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>Idealized Structure for Iron Pyrophosphate Glass [13]</td>
<td>6</td>
</tr>
<tr>
<td>1.4</td>
<td>The Structure Of Na⁺, Ca²⁺ Modified Phosphate Glass [24]</td>
<td>7</td>
</tr>
<tr>
<td>3.1</td>
<td>Composition and Glass Forming Ability of Calcium Iron Phosphate Glasses</td>
<td>16</td>
</tr>
<tr>
<td>3.2</td>
<td>XRD Pattern of the As-made CFP52 Glass Showing the Presence of Ca₂P₂O₇ Crystals</td>
<td>17</td>
</tr>
<tr>
<td>3.3</td>
<td>Density of Calcium Iron Phosphate Glasses</td>
<td>19</td>
</tr>
<tr>
<td>3.4</td>
<td>Young’s Modulus of Calcium Iron Phosphate Glasses</td>
<td>19</td>
</tr>
<tr>
<td>3.5</td>
<td>Average Thermal Expansion Coefficient between 100°C and 500°C for Calcium Iron Phosphate Glasses</td>
<td>20</td>
</tr>
<tr>
<td>3.6</td>
<td>Weight Loss of Ca-Fe-Metaphosphate (O/P=3.00) Glasses in LS at 80°C</td>
<td>21</td>
</tr>
<tr>
<td>3.7</td>
<td>Weight Loss of Ca-Fe-Polyphosphate (O/P=3.25) Glasses in LS at 80°C</td>
<td>22</td>
</tr>
<tr>
<td>3.8</td>
<td>Weight Loss of Ca-Fe-pyrophosphate (O/P=3.5) Glasses in LS at 80°C</td>
<td>22</td>
</tr>
<tr>
<td>3.9</td>
<td>Change of Lawrence Solution pH with Corrosion Time for Ca-Fe-metaphosphate (O/P=3.00) Glasses at 80°C</td>
<td>23</td>
</tr>
<tr>
<td>3.10</td>
<td>Change of Lawrence Solution pH with Corrosion Time for Ca-Fe-polyphosphate (O/P=3.25) Glasses at 80°C</td>
<td>23</td>
</tr>
<tr>
<td>3.11</td>
<td>Change of Lawrence Solution pH with Corrosion Time for Ca-Fe-pyrophosphate (O/P=3.50) Glasses at 80°C</td>
<td>24</td>
</tr>
<tr>
<td>3.12</td>
<td>XRD Result for CFP01 Glass after Reacting in LS at 80°C for 500 Hours</td>
<td>25</td>
</tr>
</tbody>
</table>
Figure 3.13.  XRD Result for CFP58 Glass after Reacting in LS at 80°C for 500 Hours........................................................................................................... 26

Figure 3.14.  Raman Spectra of CFP02 Glass before and after Immersion in LS for 1000 Hours at 80°C..................................................................................... 26

Figure 3.15.  Raman Spectra of CFP04 Glass before and after Immersion in LS for 1000 Hours at 80°C..................................................................................... 27

Figure 3.16.  Raman Spectra of CFP53 Glass before and after Immersion in LS for 1000 Hours at 80°C..................................................................................... 27

Figure 3.17.  SEM Image of CFP03 Glass Surface after Corrosion for 500 Hours in LS................................................................................................................ 29

Figure 3.18.  SEM Image of CFP27 Glass Surface after Corrosion for 500 Hours in LS................................................................................................................ 29

Figure 3.19.  SEM Image of CFP53 Glass Surface after Corrosion for 500 Hours in LS................................................................................................................ 30

Figure 3.20.  SEM Image of CFP55 Glass Surface after Corrosion for 500 Hours in LS................................................................................................................ 30

Figure 3.21.  The Infrared Spectra of CFP02 Glass Powder before and after Immersion in NaOH from 2 Hours to 20 Hours............................................................ 31

Figure 3.22.  The Infrared Spectra of CFP04 Glass Powder before and after Immersion in NaOH from 2 Hours to 20 Hours............................................................ 32

Figure 3.23.  The Infrared Spectra of CFP22 Glass Powder before and after Immersion in NaOH from 2 Hours to 20 Hours............................................................ 32

Figure 3.24.  The Infrared Spectra of CFP53 Glass Powder before and after Immersion in NaOH from 2 Hours to 20 Hours............................................................ 33

Figure 3.25.  The Infrared Spectra of CFP55 Glass Powder before and after Immersion in NaOH from 2 Hours to 20 Hours............................................................ 33

Figure 3.26.  The Infrared Spectra of CFP03 Glass Powder before and after Immersion in LS and NaOH Solutions for 20 Hours.................................................... 34

Figure 3.27.  The Infrared Spectra of CFP53 Glass Powder before and after Immersion in LS and NaOH Solutions for 20 Hours.................................................... 35
Figure 3.28. XRD Result for CFP54 Glass after Immersion in NaOH at 80°C for 20 Hours

Figure 3.29. Surface Corrosion Products Identified by XRD on Glasses after Reactions.

Figure 3.30. Chromatograms for NaOH Solutions after Immersion of Different Glasses for 8 Hours at 80°C

Figure 3.31. Total Concentration of Phosphate Released into NaOH Solution at 80°C

Figure 4.1. Classification of Ca-iron-phosphate Glass Compositions.

Figure 4.2. Equilibrium Modeling of Predominant Calcium Phase for CFP Glass in LS Solution

Figure 4.3. Equilibrium Modeling of Predominant Iron Phases for CFP Glass in LS Solution

Figure 4.4. Dissolution Rates of Glasses which are Immersed in LS for 48 Hours at 80°C Depend on the Compositions

Figure 4.5. Dissolution Rates of Glasses which are Immersed in LS for 500 Hours at 80°C Depend on the Compositions

Figure 4.6. pH Values of LS Solutions in which Glasses Immersed for 500 Hours at 80°C Depend on the Compositions

Figure 4.7. Dissolution Rates of Glasses vs. pH of LS after 500 Hours at 80°C
LIST OF TABLES

Table 2.1. Batched Compositions (mole %) of CaO-Fe₂O₃-P₂O₅ Glasses ...................... 12

Table 3.1. Properties of Calcium Iron Phosphate Glasses ............................................... 18

Table 3.2. EDS Analyses from As-made Glass Surfaces and Corroded Glass Surfaces (after 500 hours in LS) .......................................................... 31
1. INTRODUCTION

Glass fiber-reinforced cement composites have been used for nonstructural building materials since the early 1970s [1]. In general, the fibers greatly increase the flexural strength of composites relative to unreinforced cement. However, glass fiber-reinforced cement composites tend to lose strength as a result of the reaction between the highly alkaline cement matrix and the glass fibers [2].

The recent discovery of iron phosphate glasses with low melting temperatures (between 1100°C to 1200°C), outstanding corrosion resistance and continuous fiber pulling ability has attracted much interest [3-4]. However, the main challenge phosphate glasses face for the cement reinforcement application is to improve the chemical durability in high pH cement environment. Researchers found that some phosphate glass compositions can be made to be highly durable [5]. The main concern of this project is to study the properties of calcium-iron-phosphate glasses and the corrosion mechanism of the phosphate glasses in cement environments.

1.1. CORROSION STUDIES OF CEMENT REINFORCEMENT GLASS FIBERS

The cement porewater environment is typically a highly alkaline environment. The ordinary cement consists of calcium oxide, silicon oxide and smaller quantities of aluminum, iron, magnesium, and potassium oxides. Upon hydration, the cement hardens into its gel phase with by-products of calcium hydroxide, sodium hydroxide and potassium hydroxide [6]. These hydroxides remain in solution with the concrete porewater and contribute to the high pH of the porewater [7].
The decomposition of silicate glasses in high pH aqueous environment has been studied by a number of investigators [5, 8-11]. These studies reveal that most silicate glasses are decomposed at pH>10 [8]. Budd suggested that the polarity of the strong siloxane bond and the positive charge residing on the silicon atom makes the bond susceptible to attack by hydroxyl ions. The nucleophilic attack on the silicon atom initiates the attack of hydroxyl ions on the glass network. This reaction proceeds in three stages [9]:

\[
\text{Si-O-Si} \rightarrow \text{Si-•O}\ddagger \rightarrow \text{Si} + \overset{\ddagger}{\text{O}}-\text{Si} \\
\text{OH}^- \quad \text{OH}^\ddagger \quad \text{OH} \\
\text{Initial stage} \quad \text{Transition} \quad \text{Final}
\]

Scarinci et al. found that the formation of an adherent surface layer of reaction product can act as a protective coating and decrease the rate of further corrosion [10]. Therefore the relative permeability of the coating towards the diffusion of ionic species would become the rate determining step in hindering further corrosion. As for alkaline resistant (AR) glass fibers, the addition of ZrO₂ increases the corrosion resistance of glass immersed in cement environment by forming a thin, stable, passivating layer on the surface. However, this layer cannot prevent further depletion of SiO₂ and the penetration of hydroxyl ions [11]. Yilmaz et al. suggested that the corrosion of AR glass in a NaOH solution proceeds in three steps: dissolution of glass and formation of Zr-rich insoluble layer; further but slower dissolution of glass and thickening of Zr-rich layer; crack in the layer and attack on new glass surface [8].
1.2. PHOSPHATE GLASS STRUCTURE AND PROPERTIES

1.2.1. Glass Forming and Fiber Pulling Ability The addition of certain metal oxides which are not glass forming oxides can hinder glass formation while other oxides have a minimal effect [12]. Yu et al. found that increasing Fe$_2$O$_3$ and soda content in phosphate glasses could increase melting temperature as well as the tendency for devitrification [13].

Meadowcroft et al. showed that the ease of formation of several monovalent and divalent phosphate glasses could be related to the heat of formation of the solid glass [14]: when the heat of formation is small, the phosphate chains would distribute widely, and the glass would form with ease.

In general, the glass formation tendency decreases with increasing O/P ratio [15]. Brow et al. studied the glass forming ability of compositions of calcium iron phosphate glasses as shown in Figure 1.1 [16].

Phosphate glass fibers could be pulled in the temperature range with low viscosity so that they would not break off at the nozzle tip [17]. Fe-phosphate melt viscosity increases rapidly with small decreases in temperature, which makes it difficult to pull fibers from the melt without encountering some surface crystallization [18].

1.2.2. Phosphate Glass Structure. Phosphate glasses can be made with a range of structures, from a cross linked network of Q$^3$ tetrahedra to polymer-like metaphosphate chains of Q$^2$ tetrahedra to invert glasses based on small pyro (Q$^1$) and orthophosphate (Q$^0$) anions, depending on the O/P ratio as set by glass composition [19]. Figure 1.2 shows the types of different phosphate tetrahedra.
Figure 1.1. Composition of Calcium Iron Phosphate Glasses [16]. Open Circles Mean Good Glass Forming Ability, Closed Circles Represent Partially Crystallized And Crosses Represent Heavily Crystallized Compositions.

Figure 1.2. Phosphate Tetrahedral Sites that can Exists in Phosphate Glasses
It is expected that phosphate glasses with different structures would have different corrosion behavior. Marino et al. concluded that pyrophosphate glasses are relatively stable compared with other types of phosphate glasses [20].

1.2.3. Composition Effects on Glass Structure. Because the addition of appropriate modifying oxides into the parent P2O5 network can dramatically improve the physical and chemical properties [21], it is essential to understand the structural changes brought about by these network modifiers.

P2O5 network consists of corner-sharing Q⁳ PO₄ tetrahedra; each PO₄ tetrahedron has a P=O double bond. The structural instability arises from the energetic imbalance between the dπ-pπ bonding character in the terminal P=O and the bridging P-O-P configurations which tends to break up the cross-linking network [22].

Yu et al. studied the effect of iron addition on the phosphate glass structure [13]. Their XPS spectra show a gradual reduction in the concentration of bridging P-O-P bonds with increasing Fe₂O₃ concentration, which indicates that P-O-Fe (II) or P-O-Fe (III) bonds replace P-O-P bonds. The iron (II) ions are found to be in octahedral coordination, whereas the iron (III) ions are in tetrahedral and octahedral coordination or distorted octahedral coordination. Figure 1.3 shows an idealized structure of iron phosphate glass whose composition is close to the pyrophosphate which has good chemical durability [13]. Fang et al. showed that the higher Fe²⁺ ion concentration in the glass would make the glass structure closer to the crystalline Fe₃(P₂O₇)₂ [23].

Marino et al. showed that the network modifiers, like Li₂O, Na₂O, BaO, CaO and so on, offered sufficient numbers of non-bridging oxygen for the glass network, therefore those intermediates (Al₂O₃, B₂O₃ and ZnO) tended to act as glass network formers [20].
Figure 1.4 shows that adding modifiers such as Na$_2$O and CaO breaks the P-O-P bonds and creates non-bridging oxygen [24].

Figure 1.3. Idealized Structure for Iron Pyrophosphate Glass [13].

The current research focuses on CaO-Fe$_2$O$_3$-P$_2$O$_5$ glass compositions. Figure 1.3 and Figure 1.4 show that iron oxide additions can make the phosphate glass structure more cross-linked compared with calcium oxide additions. This information may be helpful in explaining the different effects of CaO and Fe$_2$O$_3$ on the phosphate glass properties.
1.2.4. **Corrosion Study of Phosphate Glass.** The rate of phosphate glass dissolution is quite dependent on the glass composition [24]. The overall dissolution processes include acid/base reactions, hydrolysis reactions and hydration reactions.

![Figure 1.4](image.jpg)

**Figure 1.4.** The Structure Of Na\(^+\), Ca\(^{2+}\) Modified Phosphate Glass [24].

The hydrolysis reaction can be expressed as follows [24]:

\[
\begin{align*}
\cdots \cdot O-P-O-P-OH + H_2O \rightarrow & \cdots \cdot O-P-OH + HO-P-OH \\
O^+Na^- & \quad O^+Na^- & \quad O^+Na^- & \quad O^+Na^-
\end{align*}
\]

P-O-P bonds break, and produce orthophosphate anions that are released into the solution [24]. However, the hydrolysis reactions only accelerate in acidic not in basic solutions. P-
O-P bonds in linear phosphate chains are shown to be as resistant to hydrolysis as Si-O-Si bonds in neutral pH solutions [25].

Bae et al. studied the effect of amount of P$_2$O$_5$ on the glass dissolution [25]. They showed that the branching Q$^3$ phosphate tetrahedra can serve as steric hindrance to the diffusion of water into the glass and consequently lower the dissolution rate. However, the strain is also introduced into the network and encourages the hydrolytic scission of the branching units. Hence, high P$_2$O$_5$ content and long Q$^2$ chains improve the glass durability. They also found that in alkaline solution, the glass dissolves non-uniformly which has greater dissolution of phosphate.

Cacaina et al. concluded that the formation of a surface layer in solution plays an important role in the glass dissolution process [26]. The surface reaction product may have a similar network molecular structure as the original glass except the modifier ions have been replaced by a hydrogen ion plus one or more water molecules. The other possibility is the layer transforms over time by localized hydrolysis and condensation reactions into a gel layer.

Hydration reactions occur at modifier cations, disrupting ionic bonds between the phosphate chains. A useful approach to improve the chemical durability of phosphate glass is to add various oxides [13]. Feng et al. built a model to quantify the relationship between glass compositions and their chemical durability [29]. They assumed the strengths of the bonds between cations and oxygens and the structural roles of the individual elements in the glass are the predominant factors in the composition dependence of the glass chemical durability. An improved structural bond strength value was calculated for glasses with different addition, which hence determined the order of
effectiveness of these oxides additions for improving glass durability. The order of increasing effectiveness is expressed as $\text{Al}_2\text{O}_3 > \text{B}_2\text{O}_3 > \text{ZrO}_2 > \text{SiO}_2 > \text{Fe}_2\text{O}_3 > \text{CaO}$.

Many researchers found the addition of iron will improve durability for phosphate glass [13, 25, 30-34]. Several researchers concluded that $\text{Fe}^{3+}$ cations can enter in the glass network with four-fold coordination and form stable $\text{P}-\text{O}-\text{Fe}$ covalent bonds and consequently increase the chemical durability [30, 31]. Yu et al. studied the relationship between iron valence and the ability of iron addition to improve glass durability [13]. The results show that the concentration of iron (II) decreases with increasing iron content and the improvement in chemical durability. This is because iron (II) and iron (III) have different roles in the structure of glasses. However, adding iron sites can pin the structure, then shorten the average polyphosphate chain length. According to the previous analyses on the mechanism and kinetics of dissolution for phosphate glass composition, the optimum O/P ratio would be close to 3.5, which corresponds to the Q$^1$ structure [15, 20]. Also, because the ferric iron has a radius of 0.64Å which is much smaller than OH- or H$_3$O$^+$ ion, iron will block the diffusion of larger hydroxonium through the modifier channels and therefore improve the chemical durability [30, 31].

Bunker et al. suggested that the divalent cation as Ca$^{2+}$ can serve as ionic cross-links between the nonbridging oxygens of two different phosphate chains, and accordingly increase chemical durability. On the other hand, when divalent cation content reaches a certain point, because the polymer chains can only accommodate a limited number of chelate cross links, there is no further increase in chemical durability [24].

Chromatographic techniques have been used to study the structure and dissolution of phosphate glasses since the 1950s [27]. The technique of high pressure liquid
chromatography (HPLC) can be used to quantitatively measure the type and distribution of phosphate tetrahedral chains and rings dissolved from the solids [28]. For most metal phosphates, HPLC provides accurate information because these solids dissolve in high pH solutions containing EDTA without breaking the bridging P-O-P bonds[28]. Sales et al. used HPLC to obtain useful information about the structure of amorphous phosphate solids, such as chain lengths and distribution of different phosphate chains, which other techniques cannot get [5, 12, 27].

1.3. SUMMARY AND THESIS STATEMENT

Low cost and superior properties have made phosphate glass a good candidate for cement reinforcement applications. The current biggest challenges are to know how phosphate glass reacts in cement environment and then to improve the chemical durability. Many researchers have studied the corrosion mechanism of phosphate glasses in neutral solution, but very few have done these studies in high alkaline environments. This thesis will explore this new area and try to answer questions about how phosphate glasses react in alkaline environments. From the previous result of compositional effects on phosphate glass structure and properties, both ferric oxide and calcium oxide can improve the chemical durability. This project will continue the study of the composition effects and do the comparison. Also, in this thesis, the effect of different phosphate chain-lengths on the glass durability will be discussed.
2. EXPERIMENTAL PROCEDURES

2.1. SAMPLE PREPARATION

Glasses were prepared from reagent grade CaCO$_3$, Fe$_2$O$_3$, and NH$_4$H$_2$PO$_4$ (Fisher Scientific Inc.). All components were weighed on a balance that provided measurements accurate to ±0.01g. Components were mixed thoroughly in aluminosilicate crucibles, and then preheated at 900°C for 1 hour in order to burn out NH$_3$ and CO$_2$. The batch materials were then melted at 1200°C for 2 hours. Melts were poured into copper molds and the glasses annealed at 450°C for 6 hours. Samples for corrosion studies were cut with a diamond saw to dimensions about 0.5×1×2cm$^3$, then polished to 600 grit finish with SiC paper on all surfaces; water was used as a lubricant.

Samples of each glass were ground using a mortar and pestle and sieved to produce powders with particle sizes in the range of approximately 125-150 μm. These particles were used for accelerated corrosion tests and infrared samples.

Glass fibers were pulled from melts to produce samples for measuring Young’s modulus. Melts were held in aluminosilicate crucibles at 1300°C for one hour, and then removed from the furnace. A silica rod was used to pull fibers from the melt surface. The glass fiber diameters were around 200μm.

Table 2.1 shows the batched compositions of glasses prepared in this study. The glasses are classified according to their O/P atom ratio, thus falling into three compositional groups: metaphosphate (O/P=3.0), polyphosphate (O/P=3.25), and pyrophosphate (O/P=3.5) glasses.
Table 2.1. Batched Compositions (mole %) of CaO-Fe$_2$O$_3$-P$_2$O$_5$ Glasses

<table>
<thead>
<tr>
<th>ID</th>
<th>O/P</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>P$_2$O$_5$</th>
<th>CaO/P$_2$O$_5$</th>
<th>Fe$_2$O$_3$/P$_2$O$_5$</th>
<th>CaO/(Fe$_2$O$_3$+CaO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFP01</td>
<td>3.0</td>
<td>50.00</td>
<td>0.00</td>
<td>50.00</td>
<td>1.00</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>CFP02</td>
<td>30.00</td>
<td>10.00</td>
<td>60.00</td>
<td>0.50</td>
<td>0.17</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>CFP03</td>
<td>16.70</td>
<td>16.70</td>
<td>66.60</td>
<td>0.25</td>
<td>0.25</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>CFP04</td>
<td>0.00</td>
<td>25.00</td>
<td>75.00</td>
<td>0.00</td>
<td>0.33</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CFP05</td>
<td>40.91</td>
<td>4.55</td>
<td>54.55</td>
<td>0.75</td>
<td>0.08</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>CFP06</td>
<td>35.71</td>
<td>7.14</td>
<td>57.14</td>
<td>0.63</td>
<td>0.13</td>
<td>0.83</td>
<td>0.83</td>
</tr>
<tr>
<td>CFP07</td>
<td>21.43</td>
<td>14.29</td>
<td>64.29</td>
<td>0.33</td>
<td>0.22</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>CFP21</td>
<td>3.25</td>
<td>60.00</td>
<td>0.00</td>
<td>40.00</td>
<td>1.50</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>CFP22</td>
<td>37.50</td>
<td>12.50</td>
<td>50.00</td>
<td>0.75</td>
<td>0.25</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>CFP23</td>
<td>27.30</td>
<td>18.20</td>
<td>54.50</td>
<td>0.50</td>
<td>0.33</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>CFP24</td>
<td>0.00</td>
<td>33.00</td>
<td>67.00</td>
<td>0.00</td>
<td>0.50</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CFP25</td>
<td>46.00</td>
<td>8.00</td>
<td>46.00</td>
<td>1.00</td>
<td>0.17</td>
<td>0.85</td>
<td>0.85</td>
</tr>
<tr>
<td>CFP26</td>
<td>15.00</td>
<td>25.00</td>
<td>60.00</td>
<td>0.25</td>
<td>0.42</td>
<td>0.38</td>
<td>0.38</td>
</tr>
<tr>
<td>CFP27</td>
<td>44.12</td>
<td>8.82</td>
<td>47.06</td>
<td>0.94</td>
<td>0.19</td>
<td>0.83</td>
<td>0.83</td>
</tr>
<tr>
<td>CFP28</td>
<td>21.43</td>
<td>21.43</td>
<td>57.14</td>
<td>0.38</td>
<td>0.38</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>CFP51</td>
<td>3.5</td>
<td>66.70</td>
<td>0.00</td>
<td>33.30</td>
<td>2.00</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>CFP52</td>
<td>50.00</td>
<td>10.00</td>
<td>40.00</td>
<td>1.25</td>
<td>0.25</td>
<td>0.83</td>
<td>0.83</td>
</tr>
<tr>
<td>CFP53</td>
<td>25.00</td>
<td>25.00</td>
<td>50.00</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>CFP54</td>
<td>0.00</td>
<td>40.00</td>
<td>60.00</td>
<td>0.00</td>
<td>0.67</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CFP55</td>
<td>43.00</td>
<td>14.00</td>
<td>43.00</td>
<td>1.00</td>
<td>0.33</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>CFP56</td>
<td>35.00</td>
<td>19.00</td>
<td>46.00</td>
<td>0.76</td>
<td>0.41</td>
<td>0.65</td>
<td>0.65</td>
</tr>
<tr>
<td>CFP57</td>
<td>14.00</td>
<td>32.00</td>
<td>55.00</td>
<td>0.25</td>
<td>0.58</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>CFP58</td>
<td>31.58</td>
<td>21.05</td>
<td>47.37</td>
<td>0.67</td>
<td>0.44</td>
<td>0.60</td>
<td>0.60</td>
</tr>
</tbody>
</table>
2.2. PHYSICAL PROPERTIES CHARACTERIZATION

Physical property measurements on glass samples included density (\( \rho \)), coefficient of thermal expansion (CTE) and Young’s modulus. Glass density was determined by the Archimedes method using DI water as the buoyancy liquid. Density was measured on two samples for each composition, with an uncertainty of \( \pm 0.003 \text{g/cm}^3 \). Thermal expansion coefficient was measured in air using an Orton 1600 dilatometer at a ramp rate of 5°C /min. The linear CTE was calculated from the length change between 100°C to 500°C for each glass. The CTE of a glass run twice varied by 5%. The glass transition temperature (\( T_g \)) and dilatometric softening temperatures (\( T_d \)) were determined from the dilatometry results. They are accurate to \( \pm 3 \text{°C} \). Young’s modulus was measured on fibers pulled from each melt using an ultrasonic acoustic pulse technique, (Panatherm 5010, Panametrics, Inc., Waltham, Massachusetts). Ten different fibers were evaluated for each composition and the average is reported.

2.3. CHEMICAL DURABILITY TESTS

Dissolution rates were measured gravimetrically on monolithic samples (two samples for each glass composition) held in Lawrence solution (LS) at 80°C for up to 1000 hours. Lawrence Solution is prepared from 0.88 g/l NaOH, 3.45 g/l KOH, and 0.48 g/l Ca(OH)\(_2\) suspended in distilled water and has a pH of approximately 13.0. It is used as a synthetic cementitious environment [34]. The glass surface area-to-solution volume ratios were set to 0.07cm\(^{-1}\). Glass powders were suspended in NaOH solution (pH=13, 0.1 molar/L) from 2 hours up to 20 hours at 80°C and the glass surface area-to-solution volume ratios were set to 0.21cm\(^{-1}\). Weight change measurements were made using a
Sartorius scale with $10^{-5}$ g resolution. The solution temperatures were maintained at 80°C to accelerate the reaction with the glass. The dissolution rates were obtained by dividing the weight loss by the surface areas and the immersion time. The pH values of the solutions were measured by the Accumet pH meter AR25. For accuracy, each dissolution experiment was repeated.

2.4. SAMPLE CHARACTERIZATION

The crystal phases of as-made glasses and corroded glasses were examined by a Scintag LET2400 X-ray diffractometer. The step rate was 0.03 deg/sec and the angles scanned were 3° to 90° 2θ. Both bulk glasses and powders were examined by XRD before and after corrosion tests.

Scanning Electron Microscopic (SEM) images were taken using the Hitachi S4700 on glass samples before and after corrosion. Standardless energy dispersive spectroscopic (EDS) analyses were performed using EDAX S-4700 ($V_{acc} = 15$ kV), and the accuracy of analyses is about 6% relative.

Raman spectra were collected from bulk glass surfaces, before and after corrosion, at Iowa State University using the Renishaw InVia Raman Microscope. The glass samples were placed horizontally at the focus of the laser beam and Raman spectra were observed at 90°. The Raman spectra were excited by 514.5 nm light from an argon ion laser. Multiple scans were made when necessary.

Corrosion reaction products were also characterized by infra-red spectrometry. Glass powders (125–150 μm) before and after corrosion in NaOH were mixed with KBr powder (about 100 mg KBr powder mixed with 2 mg glass powder). The mixture was
pressed to form a disk (~1cm diameter) using Carver 22400-227 laboratory press. Infra-red spectra were collected in the transmission mode using the Perkin Elmer 1760-x spectrometer.

High Pressure Liquid Chromatography (HPLC) experiments were done to study the phosphate anions released into solution [35]. NaOH solutions at different corrosion times are filtered by ~0.2μm filter paper and later by an Altech IC-Chelate cation filter cartridge to remove any additional free cations or particles. All the solutions were tested either fresh or refrigerated at ~3°C to stabilize the distribution of phosphate chains in solutions. The HPLC system is a modified Dionex ion chromatography system (AD25 detector and GP50 gradient pump). The effluents are 0.22M NaCl and 5mM EDTA and the reagent stream consists of a 5:1 mixture of 5.7×10⁻³ M ammonium molybdate, (NH₄)₆Mo₇O₂₄·4H₂O, in 1.8 M H₂SO₄ and 0.05 M ascorbic acid containing 5 vol% acetone. The NaCl solution concentration is progressively ramped from 5mM to 0.53mM molar after the sample injection, which causes the phosphate chains to systematically release from the column from shortest to longest. The sample stream then reacts with reagent in a custom built 10 meter long Teflon reaction coil at 150°C to form a blue solution which passes through a UV-VIS spectrometer and absorbance is measured at 660nm. Using a series of standard solutions and Beer’s Law, a calibration curve relating peak area is to PO₄ concentration was determined.
3. RESULTS

3.1. GLASS AND FIBER FORMATION

Figure 3.1 summarizes the glass forming tendencies of the compositions studied. Compositions of polyphosphate and pyrophosphate glasses containing between 40 to 60 mol% CaO were partially crystallized on their surface, whereas compositions containing more than 60 mol% were heavily crystallized. X-ray diffraction analyses (Figure 3.2) revealed that Ca$_3$P$_2$O$_7$ crystals form in several CaO-rich samples; all other compositions are amorphous, including glasses with high Fe$_2$O$_3$ contents.

![Figure 3.1. Composition and Glass Forming Ability of Calcium Iron Phosphate Glasses (Open circles indicate compositions that formed bulk glasses, closed circles represent partially crystallized compositions, and crosses represent heavily crystallized compositions. The cross-hatched area represents compositions for which fibers could be drawn from melt surface.)](image-url)
Several compositions that produce bulk glasses would not produce glass fibers from melts held at 1300°C. Fibers could be pulled from all metaphosphate (O/P=3.00) melts at 1300°C, but polyphosphates (O/P=3.25) with CaO content ≥50 mol% and pyrophosphates (O/P=3.50) with more than 14 mol% CaO did not produce homogeneous glass fibers. The cross-hatched area in Figure 3.1 shows the fiber pulling range.

![XRD Pattern of the As-made CFP52 Glass Showing the Presence of Ca$_2$P$_2$O$_7$ Crystals](image)

**3.2. PHYSICAL PROPERTIES**

Table 3.1 summarizes the physical properties that were determined for the three series of CaO-Fe$_2$O$_3$-P$_2$O$_5$ glasses. The reported data for two compositions are also shown in the Table 3.1 [16]. In general, density (Figure 3.3) and Young’s modulus (Figure 3.4) both decrease as CaO replaces Fe$_2$O$_3$ in each compositional series. In addition, the density and Young’s modulus of the glasses increase in the order metaphosphates < polyphosphates < pyrophosphates.
Table 3.1. Properties of Calcium Iron Phosphate Glasses

<table>
<thead>
<tr>
<th>ID</th>
<th>Composition molar%</th>
<th>Density g/cm³</th>
<th>T_g °C</th>
<th>T_s °C</th>
<th>CTE 10^-6/°C</th>
<th>Young’s modulus/GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO Fe₂O₃ P₂O₅</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFP-01</td>
<td>50.00 0.00 50.00</td>
<td>2.643±0.003</td>
<td>565</td>
<td>596</td>
<td>11.20</td>
<td>53.87±1.03</td>
</tr>
<tr>
<td>CP50[16]</td>
<td>50.00 0.00 50.00</td>
<td>2.71</td>
<td>550</td>
<td>NM</td>
<td>10.00</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-06</td>
<td>35.71 7.14 57.14</td>
<td>2.694±0.001</td>
<td>546</td>
<td>602</td>
<td>10.10</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-02</td>
<td>30.00 10.00 60.00</td>
<td>2.723±0.001</td>
<td>535</td>
<td>567</td>
<td>9.87</td>
<td>57.87±1.16</td>
</tr>
<tr>
<td>CFP-07</td>
<td>21.43 14.29 64.29</td>
<td>2.730±0.001</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-03</td>
<td>17.00 17.00 66.00</td>
<td>2.769±0.002</td>
<td>545</td>
<td>585</td>
<td>8.84</td>
<td>62.24±2.20</td>
</tr>
<tr>
<td>CFP-04</td>
<td>0.00 25.00 75.00</td>
<td>2.822±0.001</td>
<td>550</td>
<td>601</td>
<td>7.91</td>
<td>64.90±1.46</td>
</tr>
<tr>
<td>CFP-21</td>
<td>60.00 0.00 40.00</td>
<td>2.787±0.013</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-25</td>
<td>46.00 8.00 46.00</td>
<td>2.851±0.008</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-22</td>
<td>37.00 13.00 50.00</td>
<td>2.898±0.001</td>
<td>520</td>
<td>561</td>
<td>10.20</td>
<td>64.85±2.65</td>
</tr>
<tr>
<td>CFP-23</td>
<td>27.00 18.00 55.00</td>
<td>2.925±0.001</td>
<td>520</td>
<td>570</td>
<td>9.44</td>
<td>66.95±1.07</td>
</tr>
<tr>
<td>CFP-26</td>
<td>15.00 25.00 60.00</td>
<td>2.932±0.003</td>
<td>505</td>
<td>550</td>
<td>9.10</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-24</td>
<td>0.00 33.00 67.00</td>
<td>2.949±0.003</td>
<td>515</td>
<td>550</td>
<td>8.22</td>
<td>66.35±0.93</td>
</tr>
<tr>
<td>CFP-52</td>
<td>50.00 10.00 40.00</td>
<td>3.000±0.002</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-55</td>
<td>43.00 14.00 43.00</td>
<td>3.041±0.003</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-58</td>
<td>31.58 21.05 47.37</td>
<td>3.042±0.001</td>
<td>529</td>
<td>569</td>
<td>10.20</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-56</td>
<td>35.00 19.00 46.00</td>
<td>3.075±0.001</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-53</td>
<td>25.00 25.00 50.00</td>
<td>3.075±0.001</td>
<td>527</td>
<td>560</td>
<td>10.20</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-57</td>
<td>14.00 32.00 55.00</td>
<td>3.095±0.010</td>
<td>503</td>
<td>545</td>
<td>8.93</td>
<td>NM</td>
</tr>
<tr>
<td>CFP-54</td>
<td>0.00 40.00 60.00</td>
<td>3.085±0.005</td>
<td>499</td>
<td>519</td>
<td>9.08</td>
<td>66.84±1.48</td>
</tr>
<tr>
<td>FP40[16]</td>
<td>0.00 40.00 60.00</td>
<td>3.04</td>
<td>502</td>
<td>NM</td>
<td>7.70</td>
<td>NM</td>
</tr>
</tbody>
</table>

NM---not measured.

The coefficients of thermal expansion decrease as Fe₂O₃ replace CaO (Figure 3.5).

In general, the metaphosphate glasses have the lower CTE’s and the pyrophosphates have the greater CTE’s.
Figure 3.3. Density of Calcium Iron Phosphate Glasses

Figure 3.4. Young’s Modulus of Calcium Iron Phosphate Glasses
Figure 3.5. Average Thermal Expansion Coefficient between 100°C and 500°C for Calcium Iron Phosphate Glasses

3.3. CORROSION BEHAVIOR

3.3.1. Bulk Glass in Lawrence Solution. Figures 3.6-3.8 show the weight losses in Lawrence solution of glass monoliths versus time for the three compositional series at 80°C. In general, the initial corrosion rate is high, but decreases with time after ~200 hours. For most compositions, the glass weight does not change much after 500 hours. CFP01 (Fe-free Ca-metaphosphate) disintegrates after 500 hours and the other bulk samples stayed intact after up to 1000 hours.
The pH of Lawrence solution decreases as the phosphate glasses react, as shown in Figures 3.9 – 3.11. The extent of the pH decrease depends on the O/P molar ratio of the glasses. The metaphosphate glasses caused the greatest decrease of pH, to values from ~4 (for the iron-free glass) to ~7 (for the calcium-free glass). The final pH values (after 1000 hours) for the corroded poly and pyrophosphate series ranged from 7 to 13. Glasses with greater CaO-contents produced less change in solution pH, except for the CFP01 glass.

Figure 3.6. Weight Loss of Ca-Fe-Metaphosphate (O/P=3.00) Glasses in LS at 80°C
Figure 3.7. Weight Loss of Ca-Fe-Polyphosphate (O/P=3.25) Glasses in LS at 80°C

Figure 3.8. Weight Loss of Ca-Fe-pyrophosphate (O/P=3.5) Glasses in LS at 80°C
Figure 3.9. Change of Lawrence Solution pH with Corrosion Time for Ca-Fe-metaphosphate (O/P=3.00) Glasses at 80°C

Figure 3.10. Change of Lawrence Solution pH with Corrosion Time for Ca-Fe-polyphosphate (O/P=3.25) Glasses at 80°C
Figure 3.11. Change of Lawrence Solution pH with Corrosion Time for Ca-Fe-
pyrophosphate (O/P=3.50) Glasses at 80°C

After corrosion in LS solution for 500 hours at 80°C, CFP01 glass disintegrated
and formed CaHPO₄ crystals (Figure 3.12); other glass compositions formed
Ca₅(PO₄)₃OH crystals (Figure 3.13), except for CFP04 which remained amorphous.
Polyphosphate glasses with 21mol% to 44mol% CaO and pyrophosphate with 25mol% to
32mol% CaO also formed Ca₅(PO₄)₃OH crystals on their corroded surface. CFP21 and
CFP52 glasses still have Ca₂P₂O₇ crystals on their surface after exposure to Lawrence
solutions, and the intensity of the XRD peak is greater than what was formed for the as-
made glass (Figure 3.2).

The Raman spectra of several as-made glasses and the corresponding surface
corrosion products after reacting in LS solution for 1000 hours at 80°C are shown in
Figures 3.14 – 3.16. Several compositions have distinctively different spectra after 1000
hours on test, these are identified as “type A” and “type B” spots. In the figures, the band at 1180 cm\(^{-1}\) can be assigned to symmetric PO\(_2\) stretch on Q\(^2\) tetrahedra. The vibration at 760 cm\(^{-1}\) is due to the symmetric stretch of P-O-P bridge, and the peak at 950 cm\(^{-1}\) is due to the symmetric PO\(_4\) stretch on Q\(^0\) tetrahedra. The shoulder at 1050 cm\(^{-1}\) can be assigned to symmetric PO\(_3\) stretch on Q\(^1\) tetrahedra [19]. The symmetric PO\(_2\) stretch peak for Q\(^2\) tetrahedra of all metaphosphate glasses either disappeared or is diminished after corrosion tests. The symmetric stretch of the P-O-P bridge diminished for glasses CFP02, CFP03 and CFP04 after corrosion. CFP01 glass formed PO\(_4\) orthophosphates after corrosion, while other metaphosphate glasses formed pyrophosphates.

As for pyrophosphate glasses, the symmetric PO\(_3\) stretch peak intensity for Q\(^1\) tetrahedra decreased after corrosion and the sharp peak of the symmetric PO\(_4\) stretch on Q\(^0\) tetrahedra appears. The latter peak corresponds to the orthophosphate crystal phases identified by XRD. All the pyrophosphate glasses formed sharp Q\(^0\) tetrahedra after corrosion, regardless of calcium oxide to iron oxide concentration ratio.

Figure 3.12. XRD Result for CFP01 Glass after Reacting in LS at 80°C for 500 Hours
Figure 3.13. XRD Result for CFP58 Glass after Reacting in LS at 80°C for 500 Hours

Figure 3.14. Raman Spectra of CFP02 Glass before and after Immersion in LS for 1000 Hours at 80°C
Figure 3.15. Raman Spectra of CFP04 Glass before and after Immersion in LS for 1000 Hours at 80°C

Figure 3.16. Raman Spectra of CFP53 Glass before and after Immersion in LS for 1000 Hours at 80°C
SEM images of the surfaces of selected compositions after LS corrosion tests for 500 hours are shown in Figures 3.17 – 3.20. The surface of the metaphosphate glass CFP03 is covered by a thick reaction product (Figure 3.17). Pyrophosphate CFP27 surface has a different appearance (Figure 3.18). The surface of the high iron oxide content pyrophosphate CFP53 is crowded with small particles (Figure 3.19), while the CFP55 surface seems to be selectively attacked (Figure 3.20).

EDS spectra were collected from several spots on each surface area of these samples and these results are summarized in Table 3.2. The analyzed compositions of the fresh glasses are consistent with the batched compositions of each sample. For the metaphosphate CFP03, both Ca/P and Fe/P atom ratios increase when the corroded surface is compared to the as-made surface. For the polyphosphate CFP27 and for the pyrophosphate CFP55, the Ca/P ratios on the corroded surfaces are greater than on the as-made surfaces, whereas the Fe/P ratio on the surface of the “high Fe$_2$O$_3$” pyrophosphate CFP53 is increased after corrosion.

**3.3.2. Glass Powder in NaOH Solution.** Figures 3.21 to 3.25 show representative FT-IR spectra for the phosphate glass powders after reacting in NaOH (0.1mol/L, pH=13, 80°C) from 0 hours up to 20 hours. The absorption band centered at 1280 cm$^{-1}$ is due to the (PO$_3$)$^-$ units and the band around 1090 cm$^{-1}$ corresponds to P$_2$O$_7^{4-}$ units. In addition, the PO$_4^{3-}$ anions are assigned to the band around 932 cm$^{-1}$ and the symmetric stretching of P-O-P units are assigned to the bands at 745 cm$^{-1}$. Bands at 550 cm$^{-1}$ are due to asymmetric P-O stretching modes [22, 36]. For both metaphosphate and pyrophosphate glasses, the compositions with high calcium oxide concentration have much greater tendency to form PO$_4^{3-}$ and P$_2$O$_7^{4-}$ surface species after 20 hours corrosion.
Figure 3.17. SEM Image of CFP03 Glass Surface after Corrosion for 500 Hours in LS

Figure 3.18. SEM Image of CFP27 Glass Surface after Corrosion for 500 Hours in LS
Figure 3.19. SEM Image of CFP53 Glass Surface after Corrosion for 500 Hours in LS

Figure 3.20. SEM Image of CFP55 Glass Surface after Corrosion for 500 Hours in LS
in NaOH. The composition with high iron oxide concentration loses the main structural features more rapidly than high calcium oxide compositions. For example, compare the spectra in Figures 3.21 and 3.22 or compare the spectra in Figures 3.24 and 3.25.

Table 3.2. EDS Analyses from As-made Glass Surfaces and Corroded Glass Surfaces (after 500 hours in LS)

<table>
<thead>
<tr>
<th>ID</th>
<th>Batched composition</th>
<th>Original surface area</th>
<th>Original surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe/P</td>
<td>Ca/P</td>
<td>Fe/P</td>
</tr>
<tr>
<td>CFP03</td>
<td>0.25</td>
<td>0.13</td>
<td>0.28±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.43±0.01</td>
</tr>
<tr>
<td>CFP27</td>
<td>0.19</td>
<td>0.47</td>
<td>0.20±0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.22±0.05</td>
</tr>
<tr>
<td>CFP53</td>
<td>0.50</td>
<td>0.25</td>
<td>0.46±0.04</td>
</tr>
<tr>
<td></td>
<td>0.36±0.03</td>
<td></td>
<td>0.58±0.05</td>
</tr>
<tr>
<td>CFP55</td>
<td>0.33</td>
<td>0.50</td>
<td>0.36±0.03</td>
</tr>
<tr>
<td></td>
<td>0.39±0.03</td>
<td></td>
<td>1.23±0.01</td>
</tr>
</tbody>
</table>

Figure 3.21. The Infrared Spectra of CFP02 Glass Powder before and after Immersion in NaOH from 2 Hours to 20 Hours
Figure 3.22. The Infrared Spectra of CFP04 Glass Powder before and after Immersion in NaOH from 2 Hours to 20 Hours

Figure 3.23. The Infrared Spectra of CFP22 Glass Powder before and after Immersion in NaOH from 2 Hours to 20 Hours
Figure 3.24. The Infrared Spectra of CFP53 Glass Powder before and after Immersion in NaOH from 2 Hours to 20 Hours

Figure 3.25. The Infrared Spectra of CFP55 Glass Powder before and after Immersion in NaOH from 2 Hours to 20 Hours
Comparisons of phosphate structures that form on glass powders corroded in NaOH and LS for 20 hours are shown in Figures 3.26 and 3.27. Both metaphosphate and pyrophosphate glasses lose intensity of the P-O-P stretching mode when corroded in NaOH solution, but not in LS solution.

XRD results of glass powders corroded in NaOH are similar to results obtained by XRD analyses of glass bulk in LS. The Ca$_2$P$_2$O$_7$ crystal peak intensity of CFP21 and CFP52 became greater after 20 hours in NaOH. All the other glasses formed Ca$_5$(PO$_4$)$_3$OH crystals except for CFP04, CFP24 and CFP54 which formed Fe$_2$O$_3$ crystals (Figure 3.28). More glass compositions formed Ca$_5$(PO$_4$)$_3$OH crystals, including CFP01 in NaOH than in LS. Figure 3.29 summarizes the crystalline phases detected as corrosion products for both sets of experiments.

![Figure 3.26. The Infrared Spectra of CFP03 Glass Powder before and after Immersion in LS and NaOH Solutions for 20 Hours](image-url)
Figure 3.27. The Infrared Spectra of CFP53 Glass Powder before and after Immersion in LS and NaOH Solutions for 20 Hours

Figure 3.28. XRD Result for CFP54 Glass after Immersion in NaOH at 80°C for 20 Hours
Figure 3.29. Surface Corrosion Products Identified by XRD on Glasses after Reactions. (a) Bulk Samples Exposed To 80°C LS For 1000 Hours, (b) Glass Powders Exposed to 0.1M NaOH For 20 Hours (triangles represent Ca₃P₂O₇ crystals; open circles indicate amorphous materials; closed circles indicate Ca₅(PO₄)₃OH crystals; open squares represent CaHPO₄ crystals; and stars indicate Fe₂O₃ crystals).
Figure 3.30 shows the HPLC chromatographs for NaOH solutions after immersion of CFP02, CFP03, and CFP55 glass powder for 8 hours at 80°C (Solutions of CFP02 and CFP03 are diluted by 10). PO$_4^{3-}$, P$_2$O$_7^{4-}$ and P$_3$O$_{10}^{5-}$ anions are present, corresponding to P1, P2 and P3, respectively [35]. CFP03 glass dissolved the greatest concentration of PO$_4^{3-}$ anions into the solution among these three compositions, and CFP02 glass dissolved the greatest concentration of P$_2$O$_7^{4-}$ anions into the solution. The solution of CFP55 hardly had any amount of P$_2$O$_7^{4-}$ anions.

Figure 3.30. Chromatograms for NaOH Solutions after Immersion of Different Glasses for 8 Hours at 80°C
Based on the relationship between peak areas of each phosphate anion and its concentration, the calculated concentrations of total phosphate released at different corrosion stages are shown in Figure 3.31. The uncertainty of these values are within 20%. CFP55 released the lowest concentration of phosphate anions at every stage, $\sim 10^{-4}$ moles PO$_4^{3-}$/L/hour.

To summarize the corrosion results:

1) Dissolution rates in alkaline solutions decrease with decreasing phosphate chain length.

2) The composition does not make a significant difference for metaphosphate glasses for weight loss and pH change in LS.

3) CaO additions to polyphosphate and pyrophosphate glasses improve glass durability in LS and NaOH solutions compared with Fe$_2$O$_3$ addition.

4) Chromatography shows high CaO-content pyrophosphate glass does not release significant concentrations of phosphate into NaOH solutions.

5) The corroded surfaces are calcium-rich for high CaO-content poly and pyrophosphate glass, but iron-rich for high Fe$_2$O$_3$-content pyrophosphate glass.

6) Most compositions form Ca$_5$(PO$_4$)$_3$OH crystals after corrosion in LS and NaOH solutions. Iron-phosphate glasses form Fe$_2$O$_3$ crystals after corrosion in NaOH solutions but remain amorphous in LS solutions. Calcium-metaphosphate glass form CaHPO$_4$ crystal after corrosion in NaOH solutions but form Ca$_5$(PO$_4$)$_3$OH crystals in LS solutions.

7) Both Raman and IR spectra indicate that longer phosphate anions convert to orthophosphate units after corrosion.
Figure 3.31. Total Concentration of Phosphate Released into NaOH Solution at 80 °C
4. DISCUSSION

4.1. PROPERTIES

4.1.1. Glass Formation. The XRD analyses of bulk samples showed that all of the compositions have good glass forming ability except for glasses CFP21 and CFP52 which formed Ca$_2$P$_2$O$_7$ crystals upon quenching. This confirms Meadowerof’s theory that ease of formation of monovalent and divalent phosphate glasses could be related to the heat of formation of the solid glass [12, 14]. Because the heat of formation of iron phosphate (14 kJ/mol·atoms) is lower than that of calcium phosphate (55 kJ/mol·atoms), the iron phosphate chains would distribute more broadly, and Fe$_2$O$_3$-rich glasses would form more easily [12]. In addition, these results confirm the previous research that the glass formation tendency decreases with increasing O/P ratio [15].

4.1.2. Physical Properties. The density of a glass depends on molecular weight and packing volume. From Figure 3.3, it is concluded that density increases as the length of phosphate chains decreases. Compared with the CaO content, the Fe$_2$O$_3$ content will decrease the thermal expansion as shown in Figure 3.5. This is consistent with the previous research that found the addition of Fe$_2$O$_3$ leads to the formation of strong Fe-O-P bonds, which make the phosphate network much tighter and more cross-linked as shown in Figure 1.3 [4, 13, 37]. The iron additions can strengthen the cross-bonding between the polyphosphate chains and strengthen the bonding of the ends of these chains to the surrounding glass structure [5].

Figure 3.4 shows that iron oxide increases the Young’s modulus of the Ca-Fe-phosphate glasses. This is similar to the effect on thermal expansion, in which iron
additions strengthen the cross bonding between the phosphate chains and the ends of these chains to the surrounding glass structure.

4.2. CORROSION ANALYSIS

4.2.1. Dissolution Study. Bulk dissolution experiments reveal that the dissolution behavior of calcium iron phosphate glasses can be classified into three types, based on the weight loss and pH changes in LS solution (Figure 4.1).

Figure 4.1. Classification of Ca-iron-phosphate Glass Compositions.
The type I behavior is represented by the glass CFP01. This calcium phosphate glass forms CaHPO₄ crystals after 500 hours and the pH of solution decreases to as low as 4. (In NaOH solutions, CFP01 powders formed Ca₅(PO₄)₃OH crystals after 20 hours.)

Type II glasses include the CaO-rich poly and pyrophosphate compositions. These are relatively stable compositions. The weight losses after 500 hours corrosion in LS are all less than 0.03g/cm² and the pH of the LS does not change much (< 1.5 units) except for CFP21. CFP27 glass formed Ca₅(PO₄)₃OH crystals on its surface, and CFP21 and CFP52 grew more Ca₂P₂O₇ crystals.

The Fe₂O₃-rich poly and pyrophosphate glasses and Fe₂O₃-containing Metaphosphate glasses exhibit type III corrosion behavior. The weight losses after 500 hours corrosion in LS are greater between 0.06g/cm² to 0.09g/cm², and the solution pH dropped to ~7. The corrosion species on the glass surfaces were either Ca₅(PO₄)₃OH crystals or amorphous.

Figure 4.2 shows the calculated predominant calcium phases predicted to precipitate from solutions, using the equilibrium modeling software Predom2 and Medusa [38]. The aqueous environment was set to be similar to LS solution. The concentrations of other materials are based on weight loss calculations and HPLC results. These predictions show that when pH drops below ~7 and PO₄³⁻ concentration is > 0.05mol/L, the stable precipitate is CaHPO₄·₂H₂O. When pH remains above 7, there is an area where the stable solid phase is Ca₅(PO₄)₃OH. Ca₂P₂O₇ will be stable at lower PO₄³⁻ concentrations and lower pH. As for the predominant iron phases, Figure 4.3 shows that ferric oxide is the stable crystal phase above pH 7. The equilibrium phase modeling
strongly supports the experimental results for the formation of Ca₅(PO₄)₃OH crystals and Fe₂O₃ crystals, as shown in Figure 3.13 and Figure 3.28, respectively.

As shown in Figure 4.4 and Figure 4.5, the weight loss in Lawrence Solution is strongly related to CaO and Fe₂O₃ concentration in the glass. Previous studies discovered that the addition of both alkaline earth oxides, like CaO, and cross-linking agents, like Fe₂O₃ could effectively improve the glass durability [13, 19, 24, 28-32]. The reason is that both modifiers can strengthen the cross-links between the phosphate chains. Figure 4.4 and Figure 4.5 indicate that CaO improves resistance to high pH solution corrosion more than Fe₂O₃. Because the Ca-O-P bond is weaker than the Fe-O-P bond, they are easier to hydrate. However, due to the low solubility of Ca-phosphate phases, protective coating forms on the glass surface, thereby limiting the rate at which further corrosion takes place. This may be the reason why calcium can improve glass durability in high pH solutions. Figure 3.26 and Figure 3.27 confirm this hypothesis from another view. Since LS solution contains Ca²⁺ ions, it is easier to become saturated as the glass dissolves; therefore the corrosion slows because of the formation of the surface protective layer. This explains why the glass powder in LS solution reacts more slowly than in NaOH solution (Figures 3.26 and 3.27). However, the composition effects do not apply for Metaphosphate glasses, as shown in Figures 4.6 and 4.7.

**4.2.1. Corrosion Mechanism.** For type I glass (CFP01), the dissolution rate is slow for the first 200 hours (Figures 3.6, 3.9 and 4.4). However, it increases and the pH value of the solution drops to acidic after 200 hours. CaHPO₄ crystals form on glass surfaces after 500 hours corrosion.
Figure 4.2. Equilibrium Modeling of Predominant Calcium Phase for CFP Glass in LS Solution

Figure 4.3. Equilibrium Modeling of Predominant Iron Phases for CFP Glass in LS Solution
Figure 4.4. Dissolution Rates of Glasses which are Immersed in LS for 48 Hours at 80°C Depend on the Compositions

Figure 4.5. Dissolution Rates of Glasses which are Immersed in LS for 500 Hours at 80°C Depend on the Compositions
Figure 4.6. pH Values of LS Solutions in which Glasses Immersed for 500 Hours at 80°C Depend on the Compositions

Figure 4.7. Dissolution Rates of Glasses vs. pH of LS after 500 Hours at 80°C
The corrosion process depends on chain hydrolysis [24], where hydroxyl ions attack the long phosphate chains, to release orthophosphate anions and form CaHPO$_4$ crystals. The H$^+$ ions released into the solution as a result of the chain hydrolysis causes the solution pH to drop. This reaction continues, the glass continues to dissolve and solution pH decreases. Bunker et al. indicated that the rate of phosphate chain hydrolysis dissolution is accelerated in both acid and basic solutions, but more durable around pH7 [24]. This explains the CFP01 glass dissolved dramatically after the solution pH drop below 7. The main chemical reactions are shown as follows:

\[
\begin{align*}
\text{HO} - \text{P} - \text{O}^- \rightarrow \text{(PO}_4\text{)}^3^- + \text{H}^+ \\
\text{O}^- 
\end{align*}
\]

For type III glasses, XRD results showed that Ca$_5$(PO$_4$)$_3$OH crystals form on corroded surfaces, except for CFP04 which does not contain calcium oxide. However, the Raman spectra of CFP02 and CFP03 do not have PO$_4$ crystals after corrosion while CFP53 does. This means Ca$_5$(PO$_4$)$_3$OH crystals form by different ways. For metaphosphate glasses (CFP02 and CFP03), the crystals loosely attached to the surface and hence are easily peeled off. But for pyrophosphate glass (CFP53), the crystals are still attached to the surface. Comparing Figures 3.17 and 3.19, the surface of CFP03 is much more fragile than that of CFP53. This also explains why when metaphosphate glass are immersed in LS solution, the pH continues to drop until neutral, whereas the pH of
solution of CFP53glass only dropped to about 9. The surface coating protection is more effective on pyrophosphate glasses than on metaphosphate glasses. The IR results of glass powder in NaOH solution showed that CFP 02, CFP04 and CFP 53 dissolved quickly, as the main phosphate structure (P-O-P symmetric stretching and PO₃⁻ vibration) disappear after just two hours of corrosion (Figures 3.21, 3.22 and 3.24). The IR spectra (Figure 3.22) also showed that high Fe₂O₃ content compositions like CFP 04 tend to be destroyed by alkaline solutions more easily than high CaO content compositions like CFP02 (Figure 3.21). Combining with XRD results that the formation of Fe₂O₃ crystals on Fe-phosphate glasses after 20 hours corrosion in NaOH, it may be concluded that iron oxide released from corroding glass reacts with hydroxyl ions and precipitated out the Fe₂O₃ crystals, while glasses with higher concentrations of calcium oxide would form a protective Ca-phosphate coating on the glass surface. The main chemical reactions are shown as follows:

\[ 5Ca^{2+} + OH^- + (PO_4)^{3-} \rightarrow Ca_5(PO_4)_3OH \]
\[ Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \rightarrow \frac{1}{2}Fe_2O_3 + \frac{3}{2}H_2O \]

HPLC results showed that type II glass (CFP55) releases very small amounts of PO₄³⁻ to the NaOH solution; again this result confirmed the conclusion that high CaO content in pyrophosphate glass composition is helpful to form protective surface layer and hinder further reaction.

For metaphosphate glasses, the dissolution behavior does not change significantly when the CaO and Fe₂O₃ concentrations change. Both Fe³⁺ and Ca²⁺ react with the OH⁻, phosphate chain structure beaks up and releases different kinds of phosphate anions, resulting in the formation of Ca₅(PO₄)₃OH and Fe₂O₃. The reaction keeps going until the
solution pH reaches \(~7\). Most of the reaction products are loosely attached to the glass surface, whether amorphous or crystalline. Afterwards, these products break up and new glass surface is exposed to alkaline attack.

For the pyrophosphate glass, when CaO concentration is high, well-adhered \(\text{Ca}_5(\text{PO}_4)_3\text{OH}\) forms on the glass surface and very few \(\text{PO}_4^{3-}\) anions are released to the solution, indicating that a strong protective layer has formed to hinder further reaction. So iron oxides do not have much chance to participate in the reaction with alkaline solutions. EDS (Table 3.2) shows Ca/P increases after corrosion, while the Fe/P remained the same. When iron oxide concentration is high, \(\text{Fe}^{3+}\) will precipitate as \(\text{Fe}_2\text{O}_3\) (Figure 4.3).
5. CONCLUSION

1) Compared with calcium oxide addition to the phosphate glasses, iron oxide addition can improve the glass and fiber forming ability, decrease thermal expansion and increase Young’s modulus. This is because of the cross-link effect of iron oxide.

2) Dissolution rate in alkaline solution decreases with phosphate chain length.

3) Calcium oxide addition can improve glass durability in pyrophosphate glasses, the glass structure remains after corrosion, low concentration of phosphate anions are released to the solution. This is because calcium can form a protective layer of Ca₅(PO₄)₃OH on the glass surface which hinders the further reaction.

4) The effect of calcium oxide on corrosion resistance is not as remarkable in metaphosphate glasses as pyrophosphates. Most metaphosphate glasses hydrolyze in high pH solution, forming orthophosphate anions and releasing H⁺ ions, which decrease the solution pH.
6. FUTURE WORK

1) Chromatography tests can be done for more compositions to analyze the release of phosphate anions into the alkaline solutions. The results can be used to study the corrosion mechanism quantitively.

2) Other elements can be added to the glass composition to produce glass fibers with high mechanical strength as well as high chemical durability.


Jiawanjun Shi was born on Oct 3rd, 1981 in P. R. China to Yougang Shi and Xiaoxia Wang. She graduated from Tianjin University with her B.S. with major in ceramic science and engineering in June of 2003. She began her graduate work in January of 2005 at the University of Missouri-Rolla and received an M.S. in Ceramic Engineering in December of 2007.