

FINAL TECHNICAL REPORT

PROJECT TITLE: High-Strength / High-Alkaline Resistant Fe-Phosphate Glass Fibers as Concrete Reinforcement

DOE Award Number: DE-FC36-04GO14046

Project Period: May 1, 2004 to December 31, 2007

Principal Investigator: Mariano Velez, (573) 364-2338; mvelez@mo-sci.com

Recipient: MO-SCI Corporation
4040 Hypoint Dr.,
Rolla, MO 65401
(573) 364-2338; (573) 364-9589 FAX; www.mo-sci.com

Subcontractors: Richard K. Brow, (573) 341-6812; brow@mst.edu
Missouri University of Science & Technology
Materials Science & Engineering Department
Rolla, MO 65409

Sudhir Hublikar, (803) 643-1192; sudhir.hublikar@agy.com
AGY Holding Corporation
2558 Wagener Rd.,
Aiken, SC 29801

Partners: Tronnie Blair, (573) 302-7575; tblair@htr-group.com
HTR-Group
Lake Ozark, MO 65049

March 30, 2008

ACKNOWLEDGEMENT, DISCLAIMER AND PROPRIETARY DATA NOTICE

Acknowledgement: This report is based upon work supported by the U.S. Department of Energy under Award No. DE-FC36-04GO14046.

Disclaimer: Any findings, opinions, and conclusions or recommendations expressed in this report are those of the authors and do not necessarily reflect the views of the Department of Energy.

Proprietary Data Notice: This report contains no proprietary data or information.

TABLE OF CONTENTS

	Page
LIST OF ACRONYMS.....	4
LIST OF FIGURES.....	5
LIST OF TABLES.....	6
EXECUTIVE SUMMARY.....	7
1. INTRODUCTION.....	9
1.1. Energy Related Issues.....	9
1.2. Environmental Advantages.....	9
1.3. Cost Benefits.....	10
1.4. Commercialization Status and Plans.....	10
2. BACKGROUND	11
2.1. Mo-Sci Corporation	12
2.2. AGY Holding Corporation	12
3. EXPERIMENTAL METHODOLOGY.....	13
4. RESULTS AND DISCUSSION.....	17
4.1. Experimental Design of Ca-Fe-Phosphate Glasses.....	17
4.2. Fiberization of Ca-Fe-Phosphate Glasses.....	18
4.3. Sub-micron Size Fibers.....	19
4.4. Physical Properties.....	19
4.4.1. Thermal and Mechanical Properties.....	19
4.4.2. Bending Strength.....	22
4.5. Fiber Coating	23
4.6. Chemical Durability	24
4.6.1. Analysis of Corrosion Products on Glass Surfaces.....	25
4.7. Flexural Strength of GFRC Panels.....	27
4.8. Corrosion Testing of Metals	28
4.9. Discussion.....	29
5. ACCOMPLISHMENTS.....	32
5.1. Patents.....	32
5.2. Publications and Presentations.....	32
CONCLUSIONS.....	32
RECOMMENDATIONS.....	33
REFERENCES.....	35

LIST OF ACRONYMS

AAS: Atomic Absorption Spectroscopy
AES: Auger Electron Spectroscopy
AGY: Advanced Glass Yarns
AOC Resins: Alpha Corporation of Collierville, Tennessee
AR: Alkali Resistant
ARP: Alkaline-Resistant Phosphate
BGF: Burlington Glass Fabrics
CTE: Coefficient of Thermal Expansion
D_R: Dissolution rate
DTA: Differential Thermal Analysis
E-glass: Alumina-calcium-borosilicate glass with a maximum 2 wt.% alkali content
EDAX: Energy Dispersive Analysis of X-rays
EKIP: “Experimental K-Design” Iron-Phosphate
GFRC: Glass Fiber Reinforced Concrete
HA: Hydroxyapatite
HLW: High Level Waste
ICP: Inductively Coupled Plasma chemical analysis
IR: Infrared
K_{dis}: Glass dissolution rate in simulated lung fluid
LAW: Low-Activity Waste
LLC: Limited Liability Company
LOI: Loss On Ignition
MS&T: Missouri University of Science and Technology
O/P ratio: Oxygen/Phosphorus ratio
PCT: Product Consistency Test
PVA: Polyvinyl Alcohol
PVAc: Polyvinyl Acetate
SA/V: Sample Surface Area to solution Volume ratio
SARL: Abbreviation equivalent to private limited company in France and Italy
SBW: Sodium Bearing Waste
SEM: Scanning Electron Microscopy
SIP: “Strong” Iron-Phosphate
SIP-xxR: SIP glass with Recycled materials
SOFC: Solid Oxide Fuel Cell
T_c: Crystallization temperature
T_d: Softening temperature
TEM: Transmission Electron Microscopy
T_g: Glass transition temperature
T_L: Liquidus temperature
VHT: Vapor Hydration Test
XPS: X-ray Photoelectron Spectroscopy
XRD: X-Ray Diffraction
XRF: X-Ray Fluorescence

LIST OF FIGURES

	Page
Figure 1. Diameter of SIP-51 Ca-Fe-phosphate fiber as function of pulling speed and temperature.....	18
Figure 2. Continuous Ca-Fe-phosphate fibers manufactured at MO-SCI Corp.	18
Figure 3. Discontinuous SIP-149 Ca-Fe-phosphate fibers	19
Figure 4. DTA curves of selected Ca-Fe-phosphate glasses formulated from recycled materials	20
Figure 5. Viscosity of selected Ca-Fe-phosphate melts	21
Figure 6. Linear thermal expansion of selected Ca-Fe-phosphate glasses as function of temperature	22
Figure 7. Liquidus Temperature of selected Ca-Fe-phosphate glasses	22
Figure 8. Typical Weibull probability plot of the bending strength of Ca-Fe-phosphate fibers measured under liquid nitrogen	23
Figure 9. Chemical durability of selected bare Ca-Fe-phosphate fibers as a function of solution pH during 24 h at 80°C	24
Figure 10. Chemical durability of selected Ca-Fe-phosphate fibers in H ₂ SO ₄ at 80°C	25
Figure 11. X-Ray diffraction pattern of the corrosion product on a SIP-09 glass tile after immersion in Lawrence solution at 80°C for 500 h.....	26
Figure 12. Scanning Electron Microscopy of SIP-51 fibers as “pulled” and after immersion in Lawrence solution at 80°C for 1 month	26
Figure 13. Typical stress-strain curve of Portland cement panels reinforced with <i>bare</i> SIP-91 Ca-Fe-phosphate fibers, and <i>bare</i> Cem-FIL®	27
Figure 14. Inconel 693 coupons for corrosion test prior to testing and Ni ₃ Al coupons before and after the corrosion tests in Ca-Fe-phosphate melts	28
Figure 15. Reaction product on the surface of bare SIP-150SR Ca-Fe-phosphate glass fibers after immersion in NaOH solution for 4 days at 80°C	30
Figure 16. Composition of corrosion layers that form on the surfaces of Ca-Fe-phosphate glasses exposed to Lawrence solution at 80°C for 1000 h	31
Figure 17. Equilibrium modeling of predominant calcium phases for Ca-Fe-phosphate glasses immersed in Lawrence solution.	31

LIST OF TABLES

	Page
Table 1. Effect of Oxides on Selected Properties of Ca-Fe-Phosphate Glasses	17
Table 2. Thermal Properties of Selected Ca-Fe-Phosphate Glasses	20
Table 3. Components of Coating Solutions	23
Table 4. Flexural Strength Data for Fiber-Reinforced Cement	27
Table 5. Summary of Corrosion Tests of Metals in Contact with Ca-Fe-Phosphate Melts	28

EXECUTIVE SUMMARY

The objective of this project was to evaluate new high-strength/high alkaline-resistant Ca-Fe-phosphate glass fibers as reinforcement of Portland cement, substituting commercial silica-based alkali-resistant (AR) glass fibers. The potential benefits for substituting silica-based fibers with Ca-Fe-phosphate fibers include: (1) 40-60% lower energy usage, due to lower melting and processing temperatures; (2) extension of furnace lifetime through reduced process temperature and melting time of the phosphate glasses; and (3) less concern for health related issues associated with silica-based fibers and particulates.

MO-SCI Corp. began manufacturing Fe-phosphate glass fibers in 2002 using industrial phosphate waste from metal finishing processes as a raw material; under an SBIR contract with the U.S. Environmental Protection Agency [1]. Based on that work, a new family of Ca-Fe-phosphate glasses was developed, that have chemical durabilities, measured as weight loss in alkaline solutions (pH 13), that are superior to those of commercial AR silica-based glasses. Continuous Ca-Fe-phosphate fibers (10 to 40 μm in diameter) were pulled from platinum bushings and from specially designed ceramic bushings. Discontinuous Ca-Fe-phosphate fibers were produced by “blowing” a stream of a hot phosphate melt with an air-jet. However, the tensile strength of Ca-Fe-phosphate fibers, after exposure to Portland cement paste environments, is lower than that of current AR silicate fibers.

Because of their unusual combination of physical and chemical properties, and based on numerous inquiries received over the past years from a variety of companies, significant effort has been made to find other applications for the new Ca-Fe-phosphate fibers. Some Ca-Fe-phosphate compositions have excellent chemical resistance to strong acidic solutions (H_2SO_4 , HF), indicating potential applications where silicate-based fibers degrade quickly. One promising application involves acid-resistance Ca-Fe-phosphate fibers for hot ($\sim 260^\circ\text{C}$ / 500°F) filtration of flue gases from utility boilers and other acidic environments such as carbon black and fossil fuel burning power generation. The potential demand of such fibers is several million pounds per year – *a quantity similar to that needed for alkaline resistant fibers*. A filtration fabric simulation test is needed to assess the utility of these new fibers for the gas filtration application. The test requires ~ 200 kg of fibers to be woven into fabrics that will be mechanically exposed to hot acidic environments.

The use of phosphate fibers has several environmental advantages over the use of silica-based glass fibers: (1) furnace life extension through lower melting temperatures and shorter melting times, thus reducing refractory corrosion and refractory waste; (2) use of commercially available, inexpensive, “glass-contact” alumino-silicate refractories for glass melting instead of expensive or potentially hazardous refractories (i.e., chromia-based

refractories for E-glass); (3) lower gas emissions such as SO_x , and greenhouse gases NO_x and CO_2 , compared to conventional melting of silicate glasses; (4) reduction in melting temperature (300 to 500°C below the melting temperature of silicates) and reduction in the amount of natural gas needed for melting; and (5) less concern for health related issues that are associated with silica-based fibers and particulates. Silicate fibers have potential for silicosis. Phosphate glasses cannot cause silicosis.

It was confirmed that industrial phosphate wastes can be used as raw materials for manufacturing Fe-phosphate fibers that have excellent chemical durability in strong acidic solutions (H_2SO_4 , HF), indicating potential applications where silicate-based fibers degrade very quickly. Those phosphate wastes include materials derived from the metal finishing industry (i.e., zinc phosphating waste) and fluorescent lamp recycling.

Collaborators in this work were the Missouri University of Science & Technology (MS&T), AGY, and HTR-Group. MS&T (formerly UMR, University of Missouri-Rolla) has contributed in the development of Ca-Fe-phosphate compositions and the measurement of physical, chemical and mechanical properties; AGY has contributed technology for pulling glass fibers and in the experimental design of glasses; and HTR-Group provided Ca-phosphate powders generated in recycling fluorescent lamps as a raw material for these new glasses.

1. INTRODUCTION

The primary goal of this project was to develop alkali-resistant (AR) Ca-Fe-phosphate glass fibers for reinforcing cement products, substituting commercial AR silica-based glass fibers. It was found that some Ca-Fe-phosphate glasses have a chemical durability, measured as weight loss in alkaline solutions (pH 13), that are superior to those of commercial AR silica-based glasses in bulk form. However, the tensile strength of Ca-Fe-phosphate fibers, after exposure to Portland cement paste environments, is lower than that of current AR silicate fibers which have been coated to improve their durability.

A second goal of the project was to identify other applications where the physical and chemical properties of the new Ca-Fe-phosphate fibers may be an advantage over either inorganic or organic fibers. Some Ca-Fe-phosphate fibers have excellent chemical resistance to strong acidic solutions (H_2SO_4 , HF), indicating potential applications where silicate-based fibers degrade very quickly; e.g., acidic flue gas filtration for utility coal-fired boilers and fossil fuel burning power generation. BGF Industries, a filtration fabrics company, has verified that some Ca-Fe-phosphate fibers have a higher chemical resistance to H_2SO_4 than currently used specially-coated E-glass fibers. The potential demand of such fibers is several million pounds per year – a similar market to that of AR fibers. A test to determine the suitability of Ca-Fe-phosphate fibers for this high-temperature (260°C/500°F) filtration application is needed requiring 200 kg of fibers to be woven into a fabric for mechanical flexing while being exposed to heat and acidic environments.

1.1. Energy-Related Issues. Calcium iron phosphate glass fibers can be manufactured using the same equipment and techniques as used for silica-based fibers, but at lower temperatures: 1000 to 1200°C for fiberizing phosphates vs. 1160 to 1350°C for E-glass fibers [2] (E-glass is melted between 1370 and 1650°C). A 30-40% reduction in energy usage is estimated compared to E-glass, by a reduction of 200 to 300°C in the melting temperature, assuming that glass furnaces consume on average 12 million BTU per ton of glass in melting, 78% of which is used for melting and fiberizing [3,4]. Additional energy savings will be realized from the extended furnace lifetime resulting from reduction in process temperature, melting time, and less corrosive attack on furnace refractories. A 40-60% lower energy savings was estimated for manufacturing AR fibers: 1000 to 1200°C for phosphates vs. 1290 to 1500°C for AR silica-based fibers [5,6].

1.2. Environmental Advantages. The environmental advantages of melting and fiberizing Ca-Fe-phosphate glasses can be summarized as following:

- Extension of furnace life through lower melting temperatures and shorter melting times, thus reducing refractory corrosion.

- Potential to use commercially available, inexpensive, “glass-contact” alumino-silicate refractories instead of expensive or potentially hazardous refractories (i.e., chromia-based refractories for E-glass).
- Lower gas emissions such as SO_x , and greenhouse gases NO_x and CO_2 , compared to conventional melting of silicate glasses, due to the reduction in melting temperature (300 to 500°C below the melting temperature of silicates) and the reduction in the amount of natural gas needed for melting.
- Less concern for the health related issues that are associated with silica-based fibers and particulates (i.e., silicosis).
- Potential use of phosphate wastes as raw materials, such as those derived from the metal finishing industry and fluorescent lamp recycling.

1.3. Cost Benefits. Savings are expected from reduced glass melting furnace cost and less reliance on emission control equipment. Furnace cost is reduced by extended lifetime due to lower refractory corrosion at lower melting temperatures, reduced melting time, and/or smaller furnace requirements. The Ca-Fe-phosphate glasses can be melted in smaller furnaces (for similar glass output) since the phosphate melts are more fluid and become homogeneous 3 to 20 times faster than silica-based melts [1].

1.4. Commercialization Status and Plans. The primary goal of this project was to develop AR Ca-Fe-phosphate glass fibers to replace the commercial silica-based AR glass fibers now being used to reinforce Portland cement panels. A second goal of the project was to identify other applications where the physical and chemical properties of the new Ca-Fe-phosphate fibers would be an advantage over other fibers. Some Ca-Fe-phosphate fibers have excellent chemical resistance to strong acidic solutions (H_2SO_4 , HF), indicating potential applications where silicate-based fibers degrade very quickly; e.g., acidic flue gas filtration for utility coal-fired boilers and fossil fuel burning power generation. BGF Industries, a filtration fabrics company, has verified that some Ca-Fe-phosphate fibers have higher chemical resistance to H_2SO_4 than currently used specially-coated E-glass fibers. The current status is planning to make 200 kg Ca-Fe-phosphate fiber, which is needed to (1) test fiberizability of phosphate melts in a pilot-scale operation, and (2) manufacture a fabric for mechanical and chemical tests at BGF Industries, simulating filtration of hot gases from utility boilers and other acidic environments. MO-SCI Corp. does not have the facilities for manufacturing 200 kg of glass fiber yarns for weaving as required for the test.

2. BACKGROUND

The primary goal of this project was to determine if Ca-Fe-phosphate glass fibers could replace the current commercial AR silica-based fibers being used to reinforce Portland cement and concrete panels. Glass fiber reinforced concrete (GFRC) panels are composite materials made from a Portland cement paste, reinforced with AR glass fibers that are homogeneously dispersed throughout the cement [7,8]. These composites are used in relatively thin cross-sections such as wallboards, façades, and tiles. Such composites are lightweight construction components that provide savings in time and cost, compared to conventional cement products, when considering handling, transportation and installation. GFRCs combine the high compressive strength of cement with the high impact strength, and high tensile strength of glass fibers. The fibers reinforce the cement by increasing the flexural strength and post-cracking performance of the composite.

Current commercial AR glass fibers are high-zirconia (15 to 20 wt%) alkali-silicate compositions and are manufactured by foreign companies, including St. Gobain's Cem-FIL® (France) [5], and Nippon Electric Glass Company's NEG ARG™ (Japan) [6,9]. *However, these commercial fibers typically degrade in hydrated cement environments in about six months due to alkali attack at the glass fiber surface and to embrittlement of the fiber bundles – making GFRC products useful only for non-structural applications.* This embrittlement results from the formation of $\text{Ca}(\text{OH})_2$ crystals that bond the fiber bundles as cement hydration proceeds [10,11].

MO-SCI Corp. began manufacturing Fe-phosphate glass fibers in 2002 using industrial phosphate waste from metal finishing processes as a raw material; under an SBIR contract with the U.S. Environmental Protection Agency [1]. Iron-phosphate glasses have an outstanding chemical durability that makes them useful for nuclear waste encapsulation [12]. This nuclear waste form contains 30 to 70 wt% P_2O_5 , 25 to 50 wt% iron oxide, and smaller amounts of other oxides. A large proportion of the iron in the nuclear waste form is present as Fe^{3+} , which provides a high resistance to chemical attack in neutral and acid aqueous environments. Based on that work, a new family of Ca-Fe-phosphate glass fibers was developed that has a high chemical resistance to alkaline solutions (pH 13). Additionally, Ca-Fe-phosphate compositions were found that have excellent chemical resistance to strong acidic solutions (H_2SO_4 , HF), indicating potential applications where silicate-based fibers degrade quickly. Continuous Ca-Fe-phosphate fibers (10 to 40 μm in diameter) were pulled from platinum bushings and from specially designed ceramic bushings. Discontinuous Ca-Fe-phosphate fibers were produced by “blowing” a stream of a hot phosphate melt with an air-jet.

2.1. MO-SCI Corporation. MO-SCI Corp. serves niche markets where glasses of special compositions, sizes, shapes (solid and hollow microspheres, fibers, rods, ribbons, particles, powder), and with tailor-made properties are needed. The company's organizational structure is comprised of one corporation and two wholly owned subsidiaries (MO-SCI Specialty Products LLC and MO-SCI Health Care LLC). Starting with one product, radioactive glass microspheres which are now in commercial use to treat patients with liver cancer, MO-SCI Corp. now supplies a wide variety of glass products to over 800 customers in the US and more than 30 foreign countries. Glass products developed at MO-SCI Corp. are now widely used in the healthcare, transportation, electronics, aerospace, pharmaceutical, chemicals and sporting good industries. In addition, MO-SCI Corporation's proximity to and contractual agreements with MS&T provides it with access to the latest modern research equipment (SEM, TEM, XPS, AES, thermal analysis, XRD, ICP, AAS, rheology analysis) and technical manpower (>300 scientists and professional engineers) that are usually found at only much larger companies.

2.2. AGY Holding Corporation. AGY Holding Corp. is the reorganized corporate structure of the business formerly conducted by Advanced Glassfiber Yarns LLC and its subsidiaries. The business is now conducted through two wholly owned domestic operating subsidiaries, AGY Aiken LLC and AGY Huntingdon LLC, and its two wholly owned foreign subsidiaries AGY Europe SARL and AG Yarns Canada Inc. AGY is a worldwide supplier of glass fiber yarns used in a broad range of markets, including Automotive, Construction, Defense, Electronics, Aerospace, Marine, and Recreation.

3. EXPERIMENTAL METHODOLOGY

Two hundred and eighty Ca-Fe-phosphate glasses have been melted and evaluated for this project. Data has been collected for (1) the physical properties of those glasses, (2) the chemical-resistance of Ca-Fe-phosphate fibers in alkaline solutions (pH 13) at 80°C, neutral and acid solutions, and (3) the chemical and mechanical behavior of Ca-Fe-phosphate fibers reinforcing Portland cement. Trial melts (70 to 100 g) of Ca-Fe-phosphate glass compositions (SIP-xx series) were prepared from mixtures of reagent grade $\text{NH}_4\text{H}_2\text{PO}_4$, Fe_2O_3 , CaCO_3 , and other chemicals. The compositions were chosen with an O/P ratio between 3.3 and 3.5 since such glasses have the best corrosion resistance [14, 15].

The phosphate batches were melted in aluminosilicate crucibles in an electrical furnace for 2 h, between 1100 and 1200°C. The melts were quenched on steel plates and the glasses were annealed for 6 h near the glass transition temperature. A D-optimal mixture experimental design was performed and analyzed statistically (Design-Expert, Stat-Ease, Minneapolis, MN 55413) for sixty of those compositions (EKIP-xx series), using nine oxide components to understand their effect on the properties of phosphate glasses. Calcium iron phosphate glass compositions were also modified using Ca-phosphate powders from fluorescent lamp recycled materials (SIP-xxR series). The following thermal and mechanical properties of the Ca-Fe-phosphate glasses were evaluated:

- **Fiberizability** by pulling fibers upward from the top surface of glass-producing melts. To obtain fibers, the Ca-Fe-phosphate batch was melted in a ceramic crucible at 1200°C for 2 h in air, and then stirred (homogenized) three times, at 30 min intervals, using a silica rod. The temperature of the melt was decreased to 1100°C after 2 h, and the melt was held at this temperature for another 30 min. The ceramic crucible containing the melt was removed from the furnace and glass fibers were drawn by hand using a silica bait rod.
- **Density of bulk samples at room temperature** (23°C) using the Archimedes method, with de-ionized water as the buoyancy fluid [16]. At least three samples were tested and the average and standard deviations are reported;
- **Young's elastic modulus**, using an acoustic pulse technique (resonance method, Panotherm 5010 with an acoustic transducer), sending 20 μ -seconds duration 200 kHz pulses on glass fibers with diameter of $200 \pm 5 \mu\text{m}$ over at least a length of 10 cm [17];
- **Bending strength of glass fibers** at liquid nitrogen temperature (77°K) in order to eliminate stress corrosion effects due to humidity in the environment [18]. The failure stress (σ_{max}) for fibers using the bending method was calculated from:

$$\sigma_{\text{max}} = 1.198E \left[\frac{d}{(D-d)} \right]$$

where E is the elastic modulus, d is the fiber diameter, and D is the faceplate separation at fracture;

- **Coefficient of thermal expansion** (CTE), between 100°C and the 500°C for “as made” glass samples, and the dilatometric softening temperature (T_d) using 25 mm long glass samples, heating in air at 3°C/min (Orton Dilatometer model 1600D); and
- **Glass transition temperature** (T_g), **crystallization temperature** (T_c), and the magnitude of the crystallization exothermic peak (peak area) from differential thermal analyses (DTA, Perkin/Elmer DTA 7). The glass powder (75 to 125 μm) was heated in high-purity alumina crucibles under flowing nitrogen gas at 10°C/min. Temperature calibration was done using indium, aluminum, and gold melting point standards.

The **chemical resistance of Ca-Fe-phosphate glasses** to different aqueous solutions (acid, neutral, basic) was evaluated and compared to E-glass and to high-zirconia, silica-based commercial Cem-FIL^{®1} glass fibers by

- Immersing Ca-Fe-phosphate glass tiles, $\sim 2 \times 1 \times 1 \text{ cm}^3$, surface area to solution volume (SA/V) $\sim 0.7 \text{ cm}^{-1}$, or fibers of selected compositions in Lawrence solution (aqueous simulated cement effluent: $\text{Ca}(\text{OH})_2$ 0.48 g/l, NaOH 0.88 g/l, KOH 3.45 g/l; pH 12.5 [19]) at 80°C for up to 2,000 h and monitoring the pH of the solution and weight loss of the specimens. The tiles were polished to a 600-grit finish with SiC paper, cleaned with acetone and suspended in 125 ml polypropylene bottles containing 100 ml of Lawrence solution.
- Immersing Ca-Fe-phosphate fibers in 10 weight % NaOH solution (2.6 M) at 80°C and monitoring the pH of the solution and weight loss of the fibers during 24 h;
- Immersing Ca-Fe-phosphate fibers in 30 weight % KOH solution (6.7 M) at 80°C and monitoring the pH of the solution and weight loss of the fibers during 24 h; and
- Immersing Ca-Fe-phosphate fibers, 10 to 40 μm diameter, in neutral and acid solutions (10 wt.% H_2SO_4 and in 10 wt.% HF at 23°C and at 80°C).

The bare fibers (15 to 40 micron diameter, 5 cm long) were held in loose bundles with a plastic holder, washed with de-ionized water and dried at 80°C for 12 h, before immersion in the test solutions. The SA/V ratio for immersing fibers was $\sim 11.4 \text{ cm}^{-1}$. After testing, the fibers were removed and rinsed with de-ionized water, dried at 80°C for 12 h. Duplicate measurements were made for each glass composition and the average dissolution rate (D_R), normalized to the surface area and the corrosion time, was calculated from the weight loss. The chemical durability of selected Ca-Fe-phosphate glass powders (300 to 500 μm) was also tested, increasing the specific surface area in contact with the solution [20].

¹ Cem-FIL[®] is a Registered Trade Mark of Saint-Gobain/Vetrotex, its composition in weight % is SiO_2 62, Na_2O 14.8, CaO 6.5, TiO_2 0.1, ZrO_2 16.7 and Al_2O_3 0.8 [5].

Several polymer coatings (Section 4.5) were applied to the Ca-Fe-phosphate fibers. Coatings are commonly used in the fiberglass industry for silica-based fibers. Un-coated (bare) and polymer-coated Ca-Fe-phosphate fibers were evaluated for their chemical resistance in basic aqueous solutions at 80°C and compared to Cem-FIL® fibers.

The reaction products were analyzed by optical microscopy, SEM (Hitachi S-4700 Field Emission SEM equipped with EDAX), X-ray fluorescence (XRF, Spectro X-Lab 2000) and X-ray diffraction (XRD, Scintag XDS2000). Corrosion layers on bulk glass samples were characterized using a thin film XRD Phillips X'Pert Thin Film Diffractometer (Model PW3040/60) in continuous mode between 10° and 90°. Infrared absorption (IR, Perkin-Elmer 1760X FT-IR spectrometer) was used to detect surface reaction products after immersion in the NaOH and KOH solutions. Some Ca-Fe-phosphate fibers, such as SIP-59 and SIP-60, changed color, from dark green to brown, when immersed in the Lawrence solution for 200 h at 80°C, indicating a chemical reaction. Mössbauer spectroscopic analyses (ASA 600 spectrometer with a 50 mCi Co-57 source embedded in a Rh matrix [21-23]) of as-pulled fibers and fibers after 500 h in Lawrence solution were used to reveal a change in the iron valence which explained the color change.

The Ca-Fe-phosphate glasses that showed good chemical resistance to basic solutions, compared to silicate glasses, were melted in larger quantities (500 g to 2 kg) and tested for fiberization from platinum-bushings. Several Ca-Fe-phosphate glasses were blown into “wool fiber” (sub-micron size diameter fibers) by melting the glass in a ceramic crucible and then pouring the melt into a high-velocity air jet (0.35 MPa/50 psi). The technique showed that fibers can be made from those melts that are difficult to fiberize from bushings.

The following additional measurements were made for Ca-Fe-phosphate glasses that showed high fiberizability potential and/or high chemical resistance to alkaline solutions (pH 13):

- **Viscosity of Ca-Fe-phosphate melts** was measured as a function of temperature (850 to 1350°C) using a Brookfield rotating viscometer with a platinum spindle [24]. Each melt was thermally equilibrated at a selected temperature for 30 min, before the preheated spindle was immersed in the melt. Standard viscosity oil (117.8 poise) was used to calibrate the viscometer at room temperature. Repeated experiments gave an estimated error below ±5%;
- **Liquidus temperature** using a temperature gradient furnace and a platinum tray in which glass particles were fused to form a ~3 mm thick layer of melt [25]. The platinum tray holding the melt remained in the furnace for 24 h to ensure that equilibrium between the crystal and the melt phases was established;

- The **surface tension** of SIP-91 melts using a tube furnace and a digital video camera, from 813°C to 880°C. The measurement of the surface tension is based on the shape analysis of a sessile drop [26-28]. The surface tension of E-glass at 1300°C on a platinum-foil was measured as a control test (FTA32 Video, Version 2.0, www.firsttenangstroms.com); and
- The **tensile strength** of SIP-122 fibers was measured at room temperature (22°C) using an Instron machine (model 4302) [29].

The **flexural strength** of bare Ca-Fe-phosphate fiber-reinforced Portland cement panels was measured in a three-point loading [30]. Six specimens were prepared with nominal specimen dimensions of 22.9 cm x 5.0 cm x 1.2 cm (9"x2"x0.5") [31]. GFRC panels were also made with bare Cem-FIL[®] fibers, and with no glass fibers. The GFRC panels were prepared by mixing 2.2 volume % of fiber, 10 to 40 µm diameter, 12 mm long, with a Portland cement paste (water:cement ratio 1:3 by weight, sand:cement ratio 2:3 by weight). The GFRC samples were cured in water at 23°C during 7 and 28 days before evaluation.

The **zeta potential** and the **dielectric constant** were measured for SIP-149 sub-micron-size fibers for potential use in filtration. The zeta potential (average of 15 data points) was measured on 0.1 g/L solutions by monitoring the movement of very small particles under an electrical field (Zeta-meter 3.0 from Zeta-Meter Inc., NY). The dielectric constant as a function of frequency was measured with an Impedance Analyzer (Model HP 4194 A).

Finally, the **high-temperature corrosion of several metals** (Pt and Pt-10% Rh alloy, 304, 316, and A286 stainless steels, and Inconel 693) and Ni₃Al intermetallic coupons in phosphate melts was assessed by immersing metal coupons in melts contained in alumino-silica crucibles. The high-temperature resistant metal (Inconel 693) was chosen as it shows good chemical resistance to phosphate melts [32]. The Ni₃Al intermetallic was tested as it represents a relative new class of materials for use at high temperatures (up to 1,400°C) [33]. The corrosion test [34] used metal coupons (1.5"x0.5"x1/8") partially submerged in the Ca-Fe-phosphate melt between 900 and 1200°C. The melt was refreshed at regular time intervals and the metal coupons were weighed periodically to determine the corrosion rate.

4. RESULTS AND DISCUSSION

4.1. Experimental Design of Ca-Fe-Phosphate Glasses. A D-optimal mixture experimental design with 4 replicates at the center point was used to evaluate the main effects of nine different oxides on the properties of Ca-Fe-phosphate glasses (EKIP-xx series). The compositions were generated using 9 oxides (8 independent variables), varying P_2O_5 , from 42% to 60 mol % and an O/P ratio between 3.0 and 3.4. The objective was to find compositions with minimum dissolution rate. Sixty melts were made and the glass formation characteristics, fiberizing capability, chemical durability of glass tiles in Lawrence solution at 80°C, Young's modulus, density, glass transition temperature, softening point, and thermal expansion coefficient were measured for each composition. The analysis of the EKIP melts that produced glass indicated the effect of the different oxides on properties (Table 1): P_2O_5 increases glass fiberizability but decreases the chemical resistance; yttria, chromia, and rare earth oxides increase the chemical durability but reduce the glass forming tendency and the fiberizability; and alkaline-earth oxides increase the chemical durability. The analysis also identified design compositions with a desired set of properties. However, those compositions were not fiberizable or had dissolution rates lower than expected. The usefulness of the experimental design was limited by uncertainty in the metric used to measure corrosion resistance. In addition, the formation of Ca-hydroxyapatite crystals on the surface of CaO-rich glasses affected the weight change measurements, producing misleading predictions about the chemical stability.

Table 1. Effect of Oxides on Selected Properties of Ca-Fe-Phosphate Glasses.

Property	Best to worse
Decrease D_R (dissolution rate)	La_2O_3 or Cr_2O_3 > P_2O_5 or CaO or Fe_2O_3 or (MgO and Y_2O_3) > Y_2O_3 > MgO
Increase fiberizability	P_2O_5 > Fe_2O_3 > CaO > Cr_2O_3
Increase E (Young's modulus)	Fe_2O_3 or Cr_2O_3 > Y_2O_3 or La_2O_3 > CaO > MnO_2 > MgO > P_2O_5
Decrease density	P_2O_5 > CaO or MgO > Fe_2O_3 > Cr_2O_3 or Y_2O_3 > La_2O_3
Decrease melting temperature	P_2O_5 > MgO > CaO > NiO > Y_2O_3 > La_2O_3 > Fe_2O_3 > Cr_2O_3

4.2. Fiberization of Ca-Fe-Phosphate Glasses. Several Ca-Fe-phosphate glasses were melted in kilogram quantities and pulled into continuous fibers using platinum-bushings. The melts were pulled into continuous fibers at temperatures between 950 and 1200°C. Figure 1 shows how the diameter of SIP-51 fibers changes with pulling speed and temperature. Figure 2 shows several bundles of Ca-Fe-phosphate fibers and compared to silicate fibers (CemFIL[®] and E-glass). Some Ca-Fe-phosphate melts were also evaluated for fiberization using ceramic bushings.

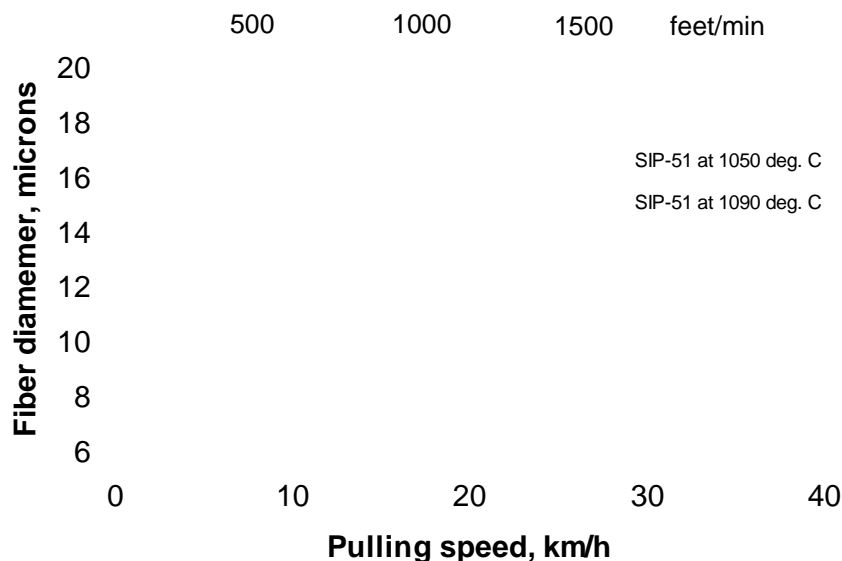


Figure 1. Diameter of SIP-51 Ca-Fe-phosphate fibers as function of pulling speed and temperature.



Figure 2. Samples of continuous Ca-Fe-phosphate fibers manufactured at MO-SCI Corp. The color is dependent upon the glass composition. The commercial silicate glasses CemFIL[®] and E-glass, are shown on the left.

4.3. Sub-micron Size Fibers. While the main effort was to produce continuous fibers, industrial sources also expressed interest in discontinuous (“wool”) fibers for several proprietary applications in filtration. The compositions SIP-129 and SIP-149 were blown into wool by melting the glass in a ceramic crucible and then pouring a thin stream of the melt into a high-velocity air jet (0.35 MPa/50 psi). The blown fiber (“wool”) was collected in a 60 cm diameter x 150 cm long (2' x 5') metal tube covered at the far end by a metal screen. The resulting fiber was between 0.5 and 20 microns in diameter with ~50% glass-shot by weight (Fig. 3). The experiment shows that “wool” fibers can be made from Ca-Fe-phosphate melts that are difficult to fiberize from bushings.

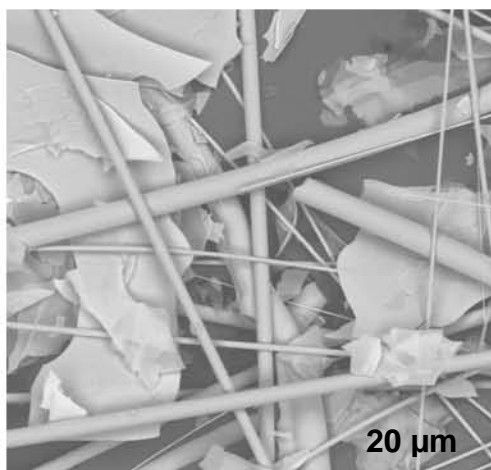


Figure 3. Discontinuous SIP-149 Ca-Fe-phosphate fibers: a mixture of fibers and flakes is observed, SEM.

4.4. Physical Properties.

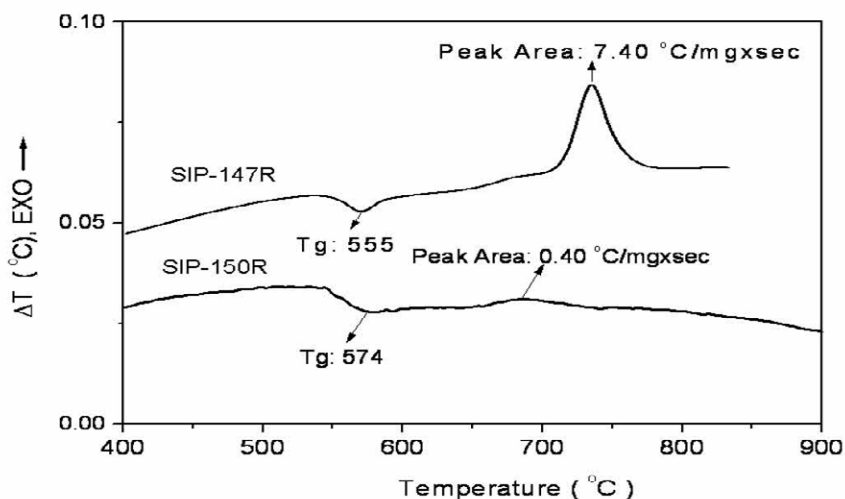
4.4.1. Thermal and Mechanical Properties. Table 2 includes the thermal and mechanical properties of selected Ca-Fe-phosphate glasses, some of which were pulled into fibers at 1200°C from the melt surface. Such collected data, together with melt viscosity and surface tension vs. temperature and DTA (Differential thermal analysis), are needed for bushing design and scaling up the fiberization process. Compositions SIP-51, SIP-55 and SIP-91 have negligible crystallization peaks in the DTA curves, and are suitable for fiberization. As an example, DTA curves for two glasses are shown in Fig. 4 to indicate the two major features in the curves: a glass transition endothermic depression between 555 and 574°C and an exothermic crystallization peak between 670 and 750°C. The fiberizability of the glass is inversely proportional to the area under the crystallization peak. For instance, composition SIP-147R has a large crystallization peak, so fibers cannot be pulled from this melt. On the other hand, fibers can be readily pulled from SIP-150R as the DTA curve from this glass shows negligible crystallization peak.

Table 2. Thermal Properties of Selected Ca-Fe-Phosphate Glasses.

Glass Code	Transition temperature T_g ($^{\circ}\text{C}$) $\pm 2^{\circ}\text{C}$	Crystallization temperature T_c ($^{\circ}\text{C}$) $\pm 2^{\circ}\text{C}$	Softening temperature T_d ($^{\circ}\text{C}$) $\pm 2^{\circ}\text{C}$	Thermal expansion coefficient CTE ($\text{ppm}/^{\circ}\text{C}$)	Density (g/cm^3)	Young's Modulus E (GPa) ± 0.5 GPa	Fiber pulling at 1200°C^*	Liquidus temperature T_L ($^{\circ}\text{C}$) $\pm 10^{\circ}\text{C}$
ARP-87 [1]	573	740	628	6.1	2.97	69.6	easy	1040
SIP-07	587	695	605	10.1	3.14	nm	not fiberizable	nm
SIP-08	610	732	627	9.9	3.13	nm	not fiberizable	nm
SIP-15	573	763	583	10.7	2.95	70.2	difficult	nm
SIP-16	600	731	647	7.3	3.00	70.0	easy	800
SIP-17	563	713	600	9.8	nm	69.7	easy	nm
SIP-19	530	724	588	10.6	2.99	71.4	difficult	1030
SIP-37	588	715	606	7.3	2.93	71.2	easy	1060
SIP-51	589	negligible peak	619	8.9	2.89	75.0	easy	1180
SIP-55	572	absent peak	577	9.1	2.83	59.0	easy	950
SIP-91	602	absent peak	605	9.5	2.84	58.4	easy	1150
SIP-99	nm	nm	610	10.8	2.98	61.5	easy	1130
SIP-108	nm	nm	610	10.8	2.98	63.5	easy	1050
SIP-115	550	720	575	10.1	2.78	52.6	easy	975
SIP-119	596	730	597	9.8	2.85	64.2	easy	1090
SIP-120	670	770	624	9.9	2.88	61.4	easy	1105
SIP-129X5	nm	830	nm	nm	3.25	70.1	difficult	1050
SIP-149	nm	870	633	nm	3.10	71.4	difficult	nm
SIP-147R	nm	740	619	10.4	3.43	nm	not fiberizable	nm
SIP-150R	nm	685	557	12.7	3.17	65.9	easy	nm

nm: not measured

*This test was done by pulling fibers upwards from the melt surface.

Figure 4. DTA curves of selected Ca-Fe-phosphate glasses formulated from recycled materials. The arrows indicate the glass transition temperature (T_g) and crystallization peaks.

It was found that Ca-Fe-phosphate glasses can be pulled into fibers when (1) the slope of the viscosity-temperature curve is relatively shallow (slope similar to the E-glass viscosity vs. temperature curve [35]), (2) the melt viscosity is between 10 and 100 poise (a lower viscosity range compared to that for silicate glasses; i.e., 100 to 1,000 poise), (3) the liquidus temperature is lower than the fiberization temperature, and (4) the exothermic crystallization peak in the DTA curve is small or absent. These facts agree with the observation that SIP-55 was the best Ca-Fe-phosphate glass to pull fibers from.

Figure 5 shows the viscosity of Ca-Fe-phosphate melts SIP-55 and SIP-91 as a function of temperature. The compositions SIP-37 and SIP-19 are included as they have very distinct viscosity-temperature relationships: SIP-37 can be fiberized at ~1150°C while SIP-19 has a steeper viscosity curve and cannot be fiberized from Pt-bushings. The composition SIP-19 was made into fibers only by pouring a stream of the molten glass (“wool manufacturing”) into an air jet. Figures 6 and 7 show, respectively, typical expansion curve and liquidus temperature measurements for selected Ca-Fe-phosphate glasses.

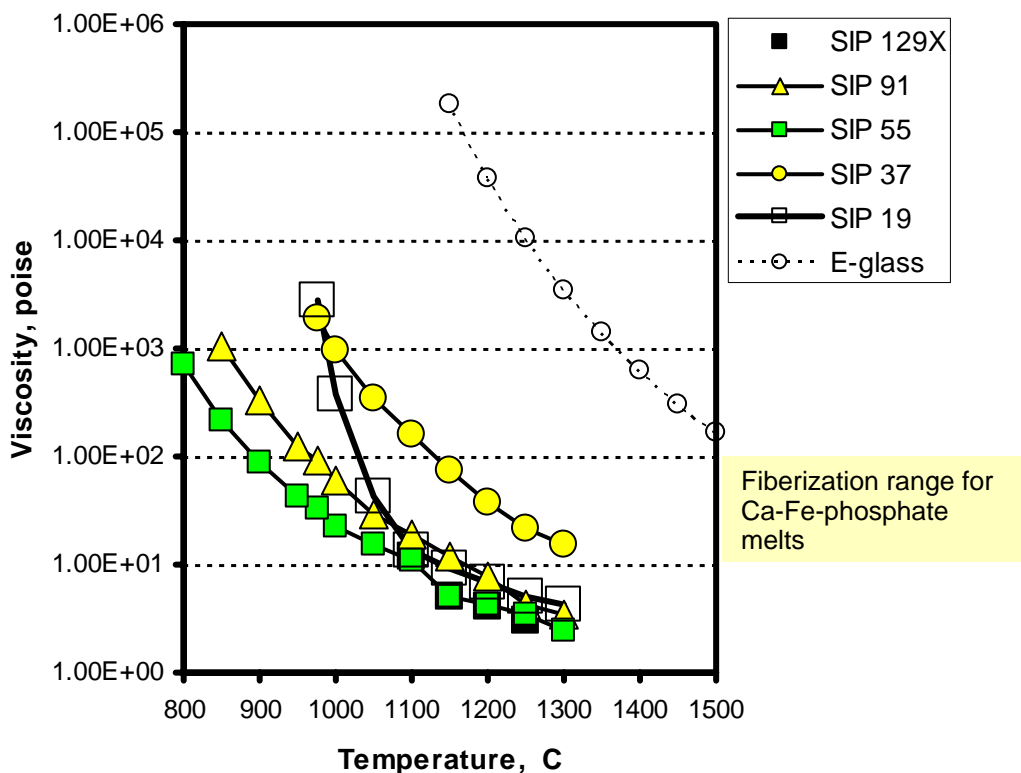


Figure 5. Viscosity of selected Ca-Fe-phosphate melts. The estimated viscosity range for pulling continuous phosphate fibers is between 10 and 100 poise. The viscosity of a typical E-glass melt [35] is included for comparison, needing to be fiberized above 1300°C (viscosities between 100 and 1000 poise for silicates).

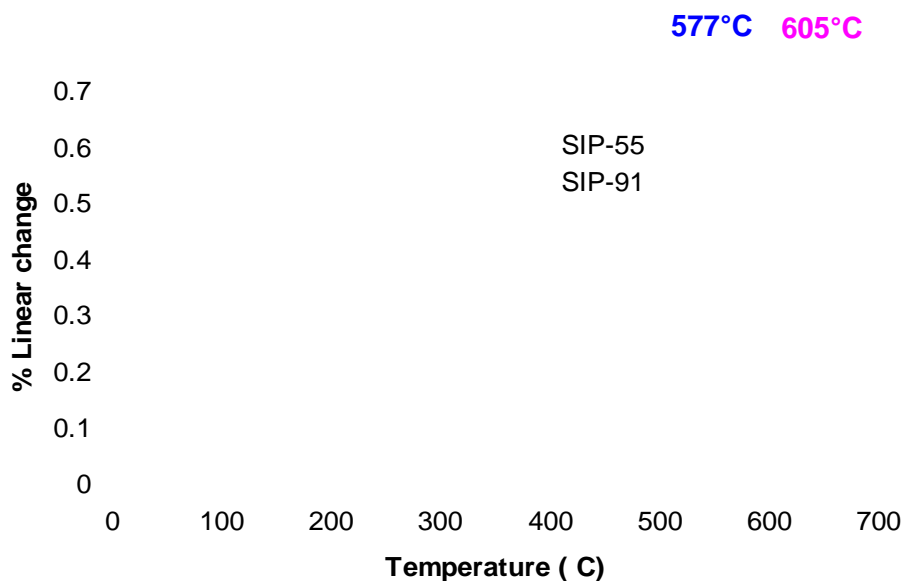


Figure 6. Linear expansion curve of selected Ca-Fe-phosphate glasses as a function of temperature, for determining the thermal expansion coefficient. Softening temperatures are shown for each glass.

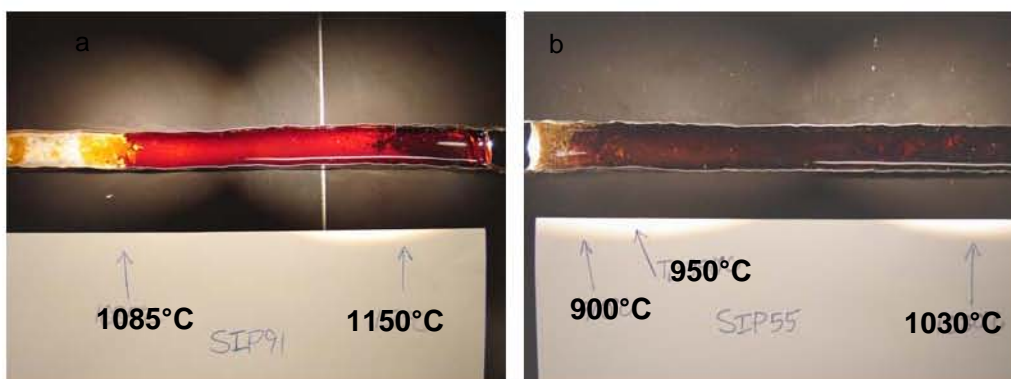


Figure 7. Liquidus Temperature of selected Ca-Fe-phosphate glasses: (a) SIP-91, determined as $1150 \pm 10^\circ\text{C}$; (b) SIP-55, determined as $950 \pm 10^\circ\text{C}$.

4.4.2. Bending Strength. Figure 8 is a Weibull probability plot of the bending strength at liquid nitrogen temperature measured for several Ca-Fe-phosphate fibers and for silica-based fibers. The Weibull modulus, m , is calculated from the slope of the least squares fitted line and is an indication of the distribution in bending strength and the nature of the flaw distribution of the glass fibers. In general, a larger Weibull modulus indicates higher quality and more reproducible fibers. The Weibull modulus for the Ca-Fe-phosphate fibers is greater than 100 which is indicative of high quality fibers (homogeneous fibers). The data also indicates that the new Ca-Fe-phosphate glass fibers possess inert bending strength (5 to 6 GPa), that are less than those obtained for silicate glass fibers (10 to 12 GPa).

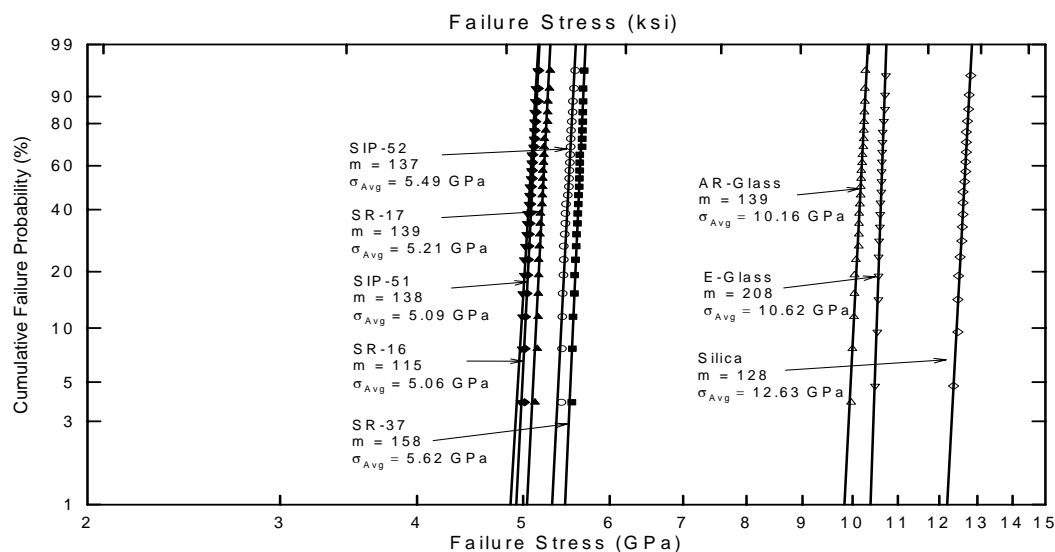


Figure 8. Typical Weibull probability plot of the bending strength of Ca-Fe-phosphate fibers measured under liquid nitrogen. The Weibull modulus (m) was calculated from the slope of the least-squares fitted line.

4.5. Fiber Coating. Several polymer coatings were applied on Ca-Fe-phosphate fibers to mechanically protect the fibers and to increase their chemical resistance. The coated fibers were tested in NaOH at 80°C and also embedded in Portland cement disks in a damp environment at room temperature. None of the coatings were resistant enough to prevent the loss in strength of the fiber after exposure to the NaOH and the Portland cement within relatively short periods of time (5 days). Most of the polymer coatings (Table 3) included only the polymer coating component, the carrier and the coupling agent. The lubricant was added to measure the tension of fibers while pulling continuously from metal bushings. Based on the 0.5 and 3 wt.% loss on ignition (LOI [36]), the coating thickness was estimated at 0.1 and 0.5 μm for a fiber diameter of $15 \pm 5 \mu\text{m}$.

Table 3. Components of Coating* Solutions.

Component function	Component Tested
Polymer coating	1. Polyvinyl alcohol (PVA), or 2. Polyvinyl acetate (PVAc), or 3. Epoxy emulsion AD503 from AOC Resins, or 4. Upaco experimental alkali-resistant polyurethanes
Carrier	Iso-propanol or water
Coupling agent	1. Hydrolyzed silane: Silquest A-187 or Dow Z6040; 0.5 to 1.5%, or 2. Kemrich organo-metallic titanates
Lubricant	1% PEG 400 MO or CAT X from ABCO Industries, Inc.

*The glass fiber industry calls this preliminary coating the “sizing” layer.

4.6. Chemical Durability. Bare (uncoated) Ca-Fe-phosphate fibers were submerged in aqueous solutions at 80°C, pH ranging from 2 to 14, to assess their chemical durability, by measuring the weight loss after 24 h (Fig. 9). The surface area to solution volume ratio (SA/V) of the fibers was 11.4 cm^{-1} , and the fiber diameter ranged from 15 to 40 μm . This information allows comparison of several Ca-Fe-phosphate compositions and the determination of their potential use for applications such as reinforcing special cements or gypsum where the pH changes as the setting reaction takes place. In such cases, a fiber is needed that is moderately resistant to low pH and highly resistant to high pH (i.e., SIP-129X5 and SIP-150R). This information should also be useful for selecting Ca-Fe-phosphate fibers for other applications that use either silicate fibers with special coatings² or asbestos³.

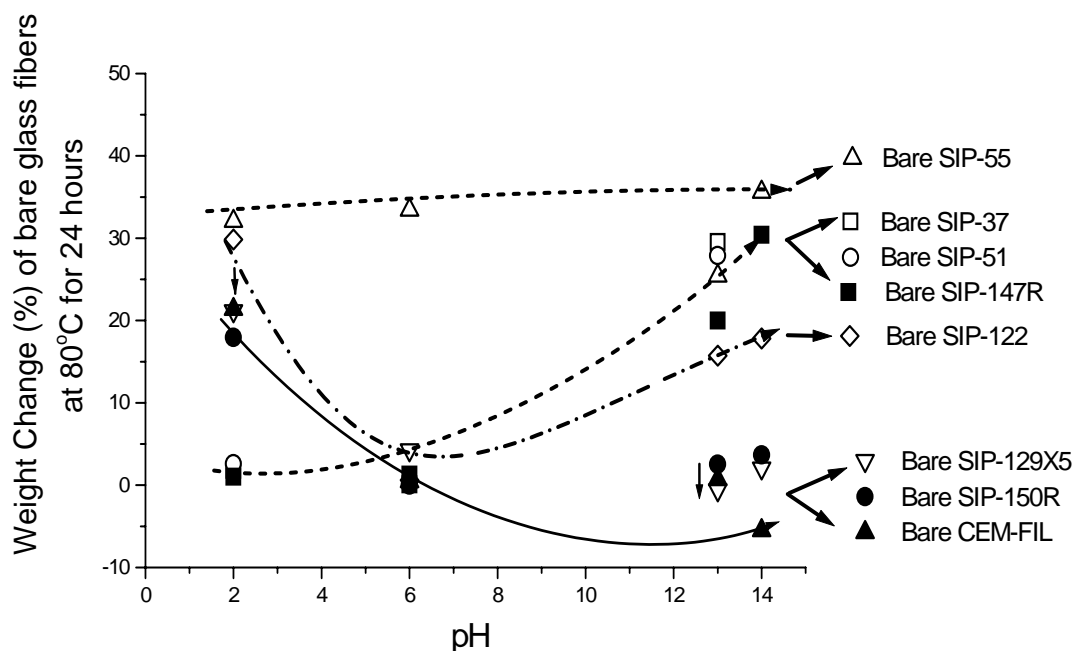


Figure 9. Chemical durability of selected bare Ca-Fe-phosphate fibers, measured as weight loss as a function of solution pH during 24 h at 80°C; SA/V~ 11.4 cm^{-1} .

² BGF Industries manufactures fabrics from silicate-based glass fiber yarns for acidic flue hot gas filtration in utility coal-fired boilers. The glass fiber yarns are encapsulated in a special graphite-silicone coating.

³ Asbestos is still in use in chlor-alkali manufacturing plants to separate chlorine, caustic soda, and in critical applications by NASA and the military.

Figure 10 shows the weight loss and change in pH for Ca-Fe-phosphate fibers immersed in 10% H_2SO_4 at 80°C. The SIP-37 fibers have better chemical durability than commercial E-glass. This indicates a potential use of Ca-Fe-phosphate fibers in bag houses for acidic flue gas filtration for utility coal-fired boilers and similar systems.

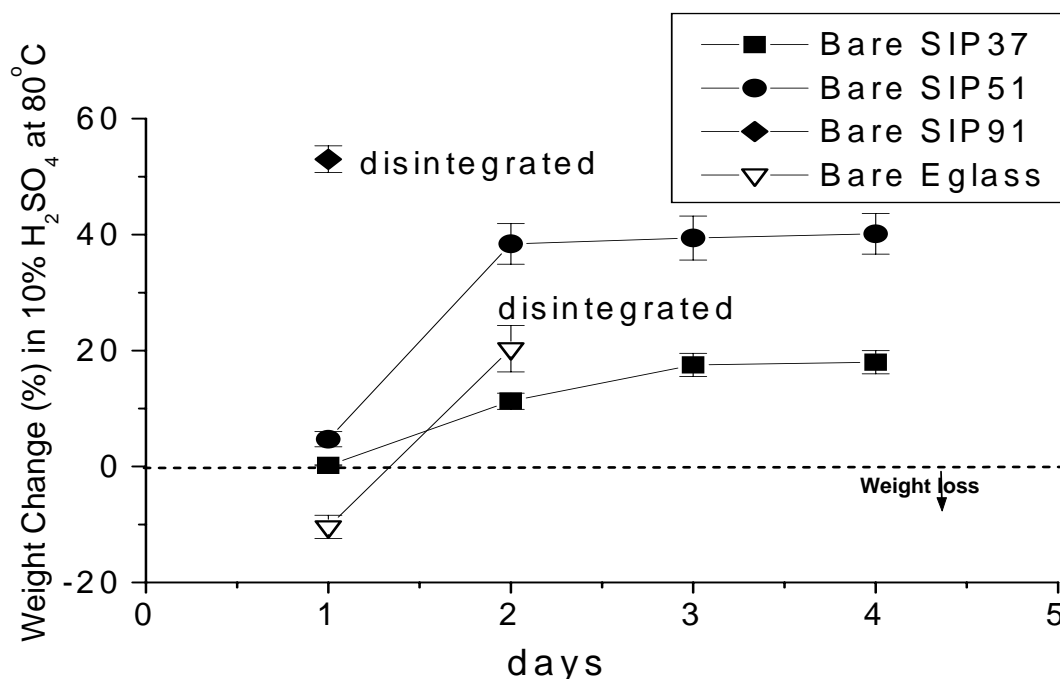


Figure 10. Chemical durability of selected Ca-Fe-phosphate fibers, measured as weight loss in 10% by weight H_2SO_4 at 80°C as function of time immersed in the solution.

4.6.1. Analysis of Corrosion Products on Glass Surfaces. Some Ca-Fe-phosphate tile specimens gained weight when immersed in Lawrence solution, which was accompanied by the formation of a white coating. X-ray diffraction analysis (XRD), thin film technique, revealed that the coating contained crystalline Ca-hydroxyapatite (HA) (Fig. 11). Figure 12a shows “as pulled” SIP-51 fibers (diameter 10 to 40 μm) and Fig. 12b shows SIP-51 Ca-Fe-phosphate fibers after being immersed in Lawrence solution at 80°C for 1 month. A Ca-hydroxyapatite layer forms on the surface of the fibers, similar to the layer found on glass tiles after immersion in Lawrence solution.

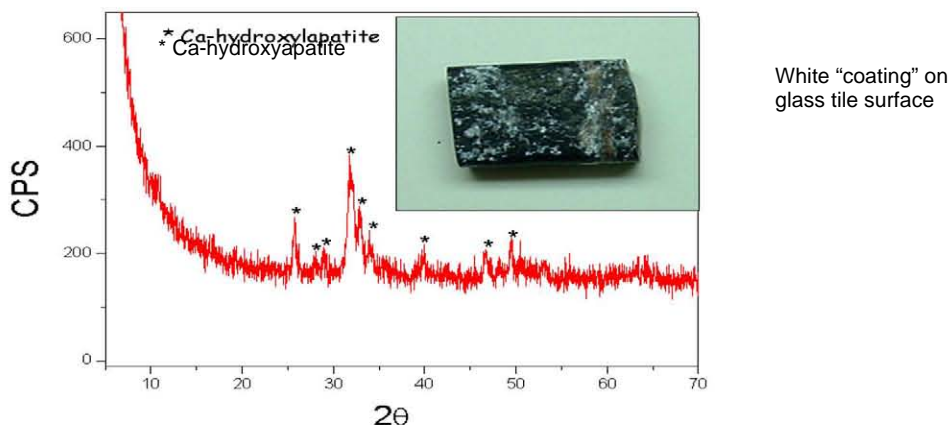


Figure 11. X-Ray diffraction pattern of the corrosion product on a SIP-09 glass tile after immersion in Lawrence solution at 80°C for 500 h. The insert is a picture of the SIP-09 tile, showing a white coating on the surface after the sample was immersed in Lawrence solution.

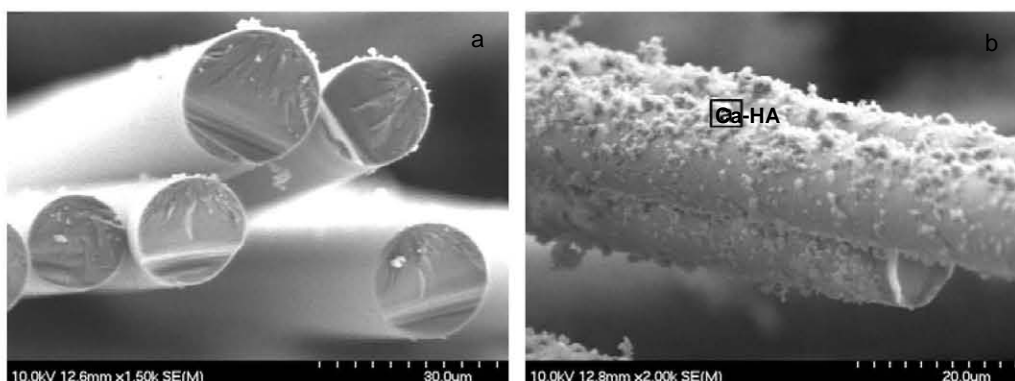


Figure 12. Scanning Electron Microscopy of SIP-51 fibers: (a) “as-pulled”, and (b) after immersion in Lawrence solution at 80°C for 1 month. The EDAX analysis of the surface layer (labeled “Ca-HA”) indicated it was Ca-hydroxyapatite.

A decrease in solution pH was observed during the basic dissolution tests, which can be explained in part by the P_2O_5 content of the glasses. In general, the decrease in Lawrence solution pH is greater as the P_2O_5 content of the glasses increases, indicating a role for the release of acidic phosphate units into solution.

Some Ca-Fe-phosphate fibers, such as SIP-59 and SIP-60, changed color from dark green to brown when immersed in the Lawrence solution for 200 h at 80°C, indicating some degree of chemical reaction. Mössbauer spectroscopic analyses of as-pulled SIP-59 fibers and fibers after 500 h in Lawrence solution revealed a change in the average iron valence that explains this color change. About 22% of the iron in the green “as-made” fibers is present as Fe^{3+} ions, whereas over 99% of the iron is present as Fe^{3+} ions in the brown fibers, after 500 h in Lawrence solution.

4.7. Flexural Strength of GFRC Panels. The flexural strength of *bare* Ca-Fe-phosphate fiber-reinforced Portland cement panels was done using a simple beam with a three-point loading [30]. The bare Ca-Fe-phosphate fibers increase the flexural strength by ~30% after 28 days curing, compared to the “fiber-free” neat Portland cement panels; a strength increase similar to that of bare Cem-FIL[®] silicate fibers with respect to neat Portland cement panels. However, the neat Portland cement panels and the bare Ca-Fe-phosphate fibers reinforced panels showed a brittle failure behavior (Fig. 13 a), while the bare Cem-FIL[®] fiber-reinforced panels showed some toughening (post-cracking performance) (Fig. 13 b). Typical flexural strength data are summarized in Table 4.

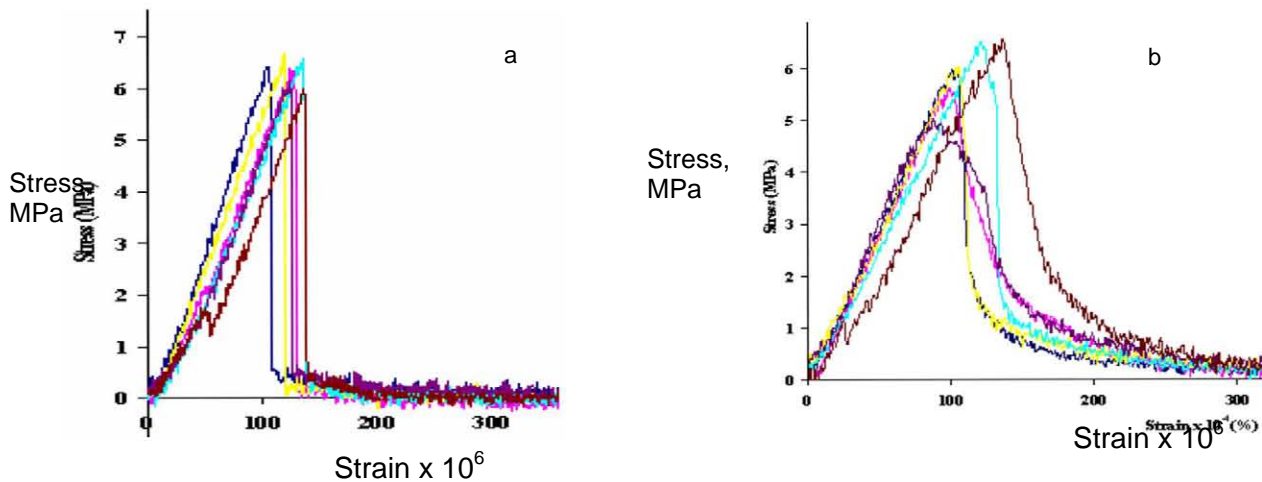


Figure 13. Typical stress-strain curve of Portland cement panels reinforced with (a) *bare* SIP-91 Ca-Fe-phosphate fibers, and (b) *bare* Cem-FIL[®], tested after curing in water for 28 days. The SIP-91 panels showed a brittle failure, similar to that of un-reinforced Portland cement panels while the Cem-FIL[®] panels showed post-cracking resistance.

Table 4. Flexural Strength Data for Fiber-Reinforced Portland Cement*

Type of reinforcing glass fiber	Ultimate Strength (MPa)	Elastic Modulus (GPa)
	at 28 days	at 28 days
Bare Cem-FIL [®] **	5.9±0.5	60±3
Bare SIP-91	6.4±0.3	64±1
Neat Cement Panel (no fiber)	4.8±0.6	66±1

*average of six samples

**Coating of commercial fiber was removed by heating at 600°C overnight.

4.8. Corrosion Testing of Metals. Glass fibers are produced by the rapid attenuation of molten glass passing through a nozzle of a metal bushing, while being continuously pulled in straight fibers. Pt-Rh alloys are used for manufacturing silicate glass fibers due to the resistance of these alloys to attack by molten glass and its stability at the temperatures needed for fiber forming [37]. There is no other known metal or alloy for bushings that can be used with silicate melts at high temperatures (1150 to 1400°C), in air, and at high humidity. As Ca-Fe-phosphate glasses melt at 200 to 300°C lower than silicates, the corrosion of different metals and alloys was evaluated to identify alternative materials for bushings. Compositions SIP-55 and SIP-91 were used for corrosion tests of different metals at temperatures close to fiberization temperatures (Table 5). The metal samples were polished with a 600 grit SiC paper and immersed in the Ca-Fe-phosphate melt at the selected temperature. Figure 14 shows metal coupons before and after the corrosion test. The tests indicate that the Ca-Fe-phosphate compositions can be melted up to 1200°C only in Pt/Rh alloy without major visual degradation.

Table 5. Summary of Corrosion Tests of Metals in Contact with Ca-Fe-Phosphate Melts.

Glass	Temperature, °C	Metal Tested	Results
SIP-55	1,000	SS304*	Complete dissolution after 3 days
		SS316	Complete dissolution after 3 days
		SSA286	Complete dissolution after 3 days
		Inconel 693	Heavy corrosion after 3 days
		Pt Wire	Complete dissolution after 1 month
		Pt/Rh 10% wire	No corrosion after 1 month
SIP-91	1,050	Inconel 693	Complete dissolution after 11 days
		Ni ₃ Al Intermetallic	Heavy corrosion after 16 h
	1,150	Inconel 693	Complete dissolution after 2 days
	1,200	Pt Wire	Complete dissolution after 7 days
		Pt/10% Rh wire	No corrosion after 7 days

* Stainless steel

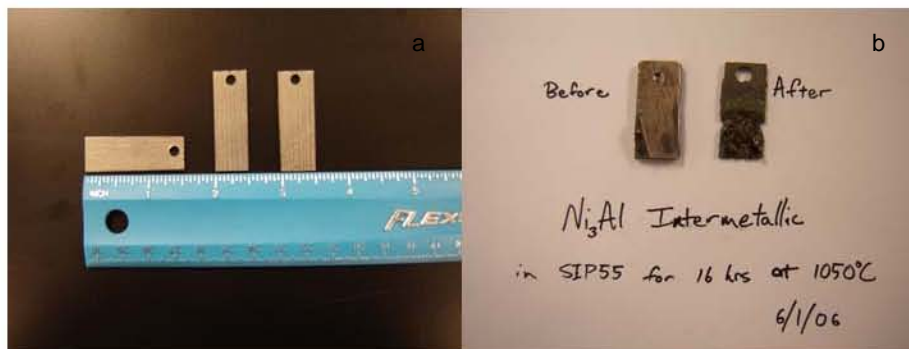


Figure 14. (a) Inconel 693 coupons for corrosion test (static) prior to testing; (b) Ni₃Al coupons before and after the corrosion tests in Ca-Fe-phosphate melts.

4.9. Discussion. Calcium iron phosphate glasses were developed, that have chemical durabilities, measured as weight loss in alkaline solutions (pH 13), that are superior to those of commercial AR silica-based glasses. Additionally, some Ca-Fe-phosphate fibers are chemically resistant to acids, including HF and 10% H₂SO₄ at 80°C (Fig. 10). This indicates a potential use of Ca-Fe-phosphate fibers in bag houses for acidic flue gas filtration for utility coal-fired boilers and similar systems.

The experimental design of compositions showed the effect of different oxides on properties of Ca-Fe-phosphate glasses: P₂O₅ increases glass fiberizability but decreases the chemical resistance; yttria, chromia, and rare earth oxides increase the chemical durability but reduce the glass forming tendency and the fiberizability; and alkaline-earth oxides increase the chemical durability. It was found that the Ca-Fe-phosphate glasses can be pulled into fibers when (1) the slope of the viscosity-temperature curve is similar to the curve for E-glass, (2) the melt viscosity is between 10 and 100 poise (a lower viscosity range compared to that for silicate glasses; i.e., 100 to 1,000 poise), (3) the liquidus temperature is lower than the fiberization temperature, and (4) the exothermic crystallization peak in the DTA curve is small or absent. These facts agree with the observation that SIP-55 was the best Ca-Fe-phosphate glass to pull fibers from. The compositions SIP-129 and SIP-149 were blown into sub-micron size fibers showing that “wool” fibers can be made from melts that are difficult to fiberize from bushings.

Calcium iron phosphate glasses either dissolved or a reaction layer formed on their surface when in contact with basic solutions (pH 13) at 80°C. The AR Ca-Fe-phosphate glasses form a reaction layer, identified as Ca-hydroxyapatite. This reaction is similar to that observed for Cem-FIL® fibers in Lawrence solution, where a reaction product layer protects the fibers from further attack. However, the formation of a corrosion layer appears to have a deleterious effect on the mechanical properties of the Ca-Fe-phosphate fibers, not seen in the bulk samples. For instance, Fig. 15 shows SIP-150R Ca-Fe-phosphate fibers, one of the most stable compositions in alkaline solutions measured as weight loss (Fig. 9), after the corrosion test in basic solutions. A reaction product has formed and appears to have initiated cracks in the fibers. The reacted fibers possess very little mechanical strength after the corrosion test. Two mechanisms of corrosion attack may be in place: one is surface dissolution, and the second is formation of a layer with the reaction products.

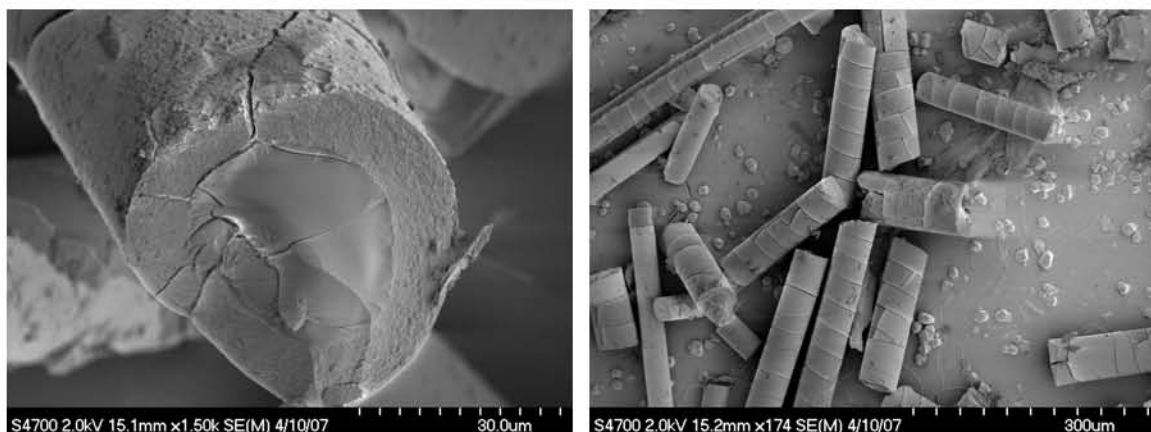


Figure 15. Reaction product on the surface of bare SIP-150R glass fibers after immersion in NaOH solution for 4 days at 80°C. The core fiber is glassy but the outer layer, mainly Ca-hydroxyapatite, is cracked which likely weakens the remaining glass core.

The type of corrosion layer that forms on glass surfaces exposed to alkaline conditions depends on the glass composition and the species in the surrounding solution. Figure 16 shows which phosphate crystals form on the surfaces of CaO-Fe₂O₃-P₂O₅ glasses exposed to 80°C Lawrence solution for 1000 h. Ca-hydroxyapatite is the dominant phase for most compositions, although an amorphous surface film forms on Fe-rich compositions, and different Ca-phosphates form on the surfaces of Ca-rich compositions. The formation of these different species suggests different corrosion mechanisms [38]. The corrosion reactions were modeled using thermodynamic calculations for the predominant phases. Figure 17 shows the results of some of these calculations, using a simulated Lawrence solution environment. The calculations indicate that Ca-hydroxyapatite, Ca₅(PO₄)₃OH, is indeed the stable phase under the alkaline conditions found in Portland cement environments.

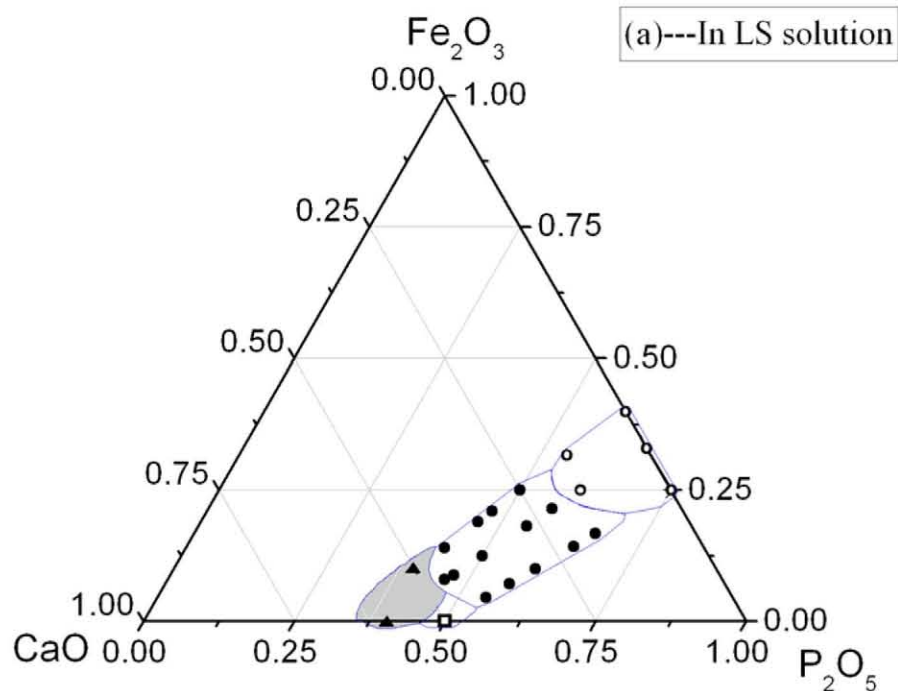


Figure 16. Composition of corrosion layers that form on the surfaces of Ca-Fe-phosphate glasses (mole%) exposed to Lawrence solution at 80°C for 1000 h. Triangles represent $\text{Ca}_2\text{P}_2\text{O}_7$ crystals; open circles indicate amorphous materials; closed circles indicate $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ crystals; open squares represent CaHPO_4 crystals.

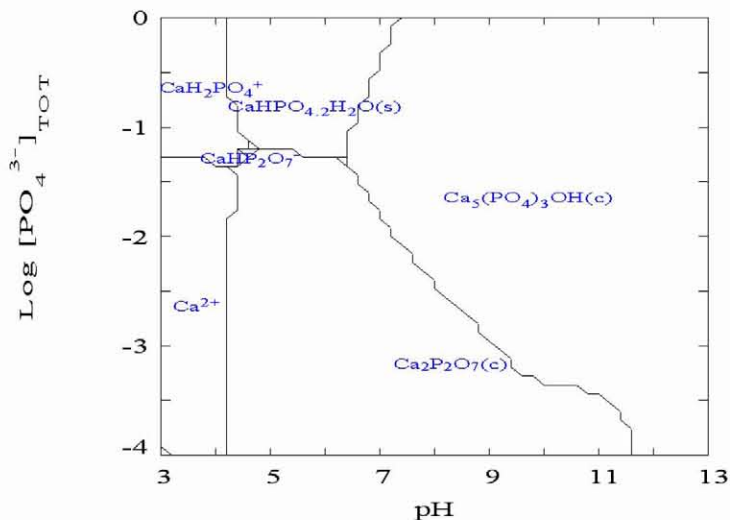


Figure 17. Equilibrium modeling of predominant calcium phases for Ca-Fe-phosphate glasses immersed in Lawrence solution.

5. ACCOMPLISHMENTS

5.1 Patents

R.K. Brow, S.T. Reis, M. Velez, D.E. Day, U.S. Patent Application No. 60/745,036, Alkaline Resistant Phosphate Glasses and Method of Preparation and Use Thereof, assigned to MO-SCI Corp., 2007.

5.2. Publications and Presentations

1. S.T. Reis, J. Shi, R.K. Brow, M. Velez, D.E. Day, Alkaline-Resistant Glass Fibers for Concrete Reinforcement, UMR-UTC Winter 2005 Newsletter, <http://campus.umn.edu/utc/newslet/vol2issue2/Newsletter3.htm>
2. J. Shi, R. K. Brow, S. T. Reis, Alkaline-Resistant Properties of Calcium-Iron-Phosphate Glasses, Spring Meeting of the Glass & Optical Materials Division of the American Ceramic Society, Greenville, SC, May 16-19, 2006.
3. J. Shi, Properties of Alkaline Resistant Calcium Iron Phosphate Glasses, M.Sc. Thesis, Ceramic Engineering, University of Missouri-Rolla, August 2007.

CONCLUSIONS

New Ca-Fe-phosphate glasses were developed whose chemical durabilities in alkaline solutions (pH 13) were comparable or superior to those of commercial AR silica-based glasses. However, the tensile strength of Ca-Fe-phosphate fibers, after being exposed to alkaline environments, including wet Portland cement pastes, is lower than that of current AR silicate fibers. The main results of the project are summarized as:

1. Developed new Ca-Fe-phosphate glasses which can be melted and processed 300 to 500°C lower than silica-based glasses. This offers the possibility of manufacturing glass fibers with lower energy costs by 40-60% and the potential to reduce manufacturing waste and lower gas emissions.
2. Found that P_2O_5 increases glass fiberizability but decreases the chemical resistance of phosphate glasses; yttria, chromia, and rare earth oxides increase the chemical durability but reduce the glass forming tendency and the fiberizability; and alkaline-earth oxides increase the chemical durability.
3. Found that Ca-Fe-phosphate melts can be pulled into fibers depending on the slope of the viscosity-temperature curve and within a viscosity range between 10 and 100 poise. Additionally, a liquidus temperature 50 to 100°C below the fiberization temperature and a small or absent crystallization peak is needed to obtain "fiberizable" compositions, as is observed for silicate melts.

4. Pulled continuous glass fibers from selected Ca-Fe-phosphate melts using multi-hole Pt/Rh bushings and ceramic bushings.
5. Fabricated discontinuous, sub-micron size, Ca-Fe-phosphate fibers by “blowing” a stream of the Ca-Fe-phosphate melt with an air-jet.
6. Developed fiberizable Ca-Fe-phosphate compositions with excellent chemical durability in strong acidic solutions (H_2SO_4 , HF), indicating potential applications where silicate-based fibers degrade very quickly.
7. Recommended the glasses SIP-37, SIP-55 and SIP-91 for scaling up the fiberization process. These compositions can be easily made into fibers at the lowest temperatures. Composition SIP-37 is chemically resistant to 10% H_2SO_4 solution at 80°C (Fig. 10) and is recommended for filtering hot acidic flue gases from electrical generating plants burning fossil fuel.

RECOMMENDATIONS

Because of the unusual combination of physical and chemical properties of phosphate glasses and phosphate fibers, several applications have been considered for phosphate fibers [i.e., 39]. It is suggested now to continue investigating the following applications of Ca-Fe-phosphate glasses and fibers:

1. *Acid resistance-applications of phosphate fibers in hot gas filtration in utility coal fired boilers:* SIP-37 fibers were sent to BGF Industries for testing in H_2SO_4 and compared to E-glass; the glass currently used for this application. In their tests, the Ca-Fe-phosphate fibers showed 10 times better chemical durability than the currently used E-glass fibers, measured from the weight loss after soaking in 10% H_2SO_4 soak at room temperature. The potential demand of this fiber is several million pounds per year, which is comparable to the quantity of AR silicate fibers being produced at this time.
2. *High chemical durability phosphate glasses for nuclear waste encapsulation:* Iron phosphate glasses can contain high nuclear waste loadings (HLW, LAW and SBW), including components which are poorly suited for borosilicate glasses, and meet all of DOE's chemical durability (PCT and VHT) requirements. Additionally, phosphate glasses can be melted in several types of furnaces [40].
3. *Phosphate glasses with high-coefficient of thermal expansion (CTE) for sealing to metals:* High CTE phosphate glasses can be used as seals between ceramics or glasses and metals in SOFCs (Solid oxide fuel cells), or as enamel coating of steels. Glasses such as SIP-154 exhibit high coefficient of thermal expansion (17.9 ppm/°C), low softening temperature (474°C), low viscosity and good chemical durability in basic

and acid environment, compared to silicate glasses [41]. The combination of unique properties makes them good sealing glasses for high-expansion and relatively low-metals, such as copper, aluminum or aluminum alloys [42].

4. Phosphate-fiber reinforcement of Mg-phosphate cements for shields in nuclear reactors: SIP-37 and SIP-51 chopped fibers were sent to Argonne National Lab (Dr. Arun Wagh). Once set, the Mg-phosphate cements have a pH between 7 and 9 depending on the fillers (loading of 2% fiber). However, since they are produced by acid-base reaction, the initial pH of the phosphate solution is 4 and during the reaction, the pH rises to become neutral.

5. Dark-colored phosphate fibers for insulation in environments below 600°C, but above the temperature where polymer fiber coatings decompose: F-40 Fe-phosphate fibers were sent to Aspen Aerogels, Northborough, MA (Kevin Horgan). There is a need for fibers that can operate at 700°C using a low cost dark glass fiber (continuous use at 650°C). The Fe-phosphate fiber is dark black/brown so it may provide some benefit in absorbing blackbody radiation (IR) which influences higher temperature thermal conductivity (their value is typically around 12-15 mW/m-K).

6. Relative lower-cost phosphate-fibers alternative for applications that currently use E-glass fibers or asbestos. The lower-cost would be achieved by using recycled materials and melting and fiberizing at temperatures below 1000°C. Phosphate fibers could replace E-glass fibers in special insulation applications. Asbestos is still being used in chlor-alkali manufacturing plants to separate chlorine, caustic soda, and hydrogen, and by NASA and the military.

7. IR and UV transmitting phosphate glasses for optical applications: Phosphate glasses have been proposed as optical materials for collecting, delivering, focusing, or amplifying light [43]. One possible use for phosphate glass may be in improved optical fibers for laser surgery. Filters for UV transmission and visible-absorbing filters are made of phosphate glasses [44].

8. Phosphate-based bioactive glass fibers: Biological active phosphate glass ceramics have been proposed for hard tissue or for bone replacement, containing between 43 and 58 wt % P_2O_5 [45]. Other P_2O_5 -containing bioactive glass compositions have been made at MO-SCI Corp. for reinforcing polymers and replacement for damaged bone [46, 47].

REFERENCES

1. T. M. Neidt, *Recycling of Industrial Phosphate Waste as Raw Material for Innovative Iron Phosphate Glass Fibers*, MO-SCI Corp., Final Report Phase I SBIR Contract No. 68-D-03-030, U.S. Environmental Protection Agency, September 30, 2003.
2. F.T. Wallenberger, J.C. Watson, H. Li, *Glass Fibers*, ASM Handbook, Vol. 21: Composites, ASM International, 2001.
3. *Glass, Industry of the Future*, DOE – Office of Industrial Technology, 2002; <http://www.nrel.gov/docs/fy02osti/32135.pdf>
4. C.P. Ross, G.L. Tincher, *Glass Melting Technology: A Technical and Economic Assessment*, M. Rasmussen (editor), DOE/GMIC, 2004.
5. K. M. Fyles, P. Shorrocks, *Alkali Resistant Glass Fibers for Cement Reinforcement*, U.S. Patent 4,345,037, 1982, assigned to Pilkington Brothers Ltd (GB).
6. Kanebo Ltd. and Nippon Electric Glass Company Ltd., *Alkali Resistant Glass Composition and Alkali Resistant Glass Fibers Prepared Therefrom*, British Patent 1,548,776, 1979.
7. F.W. Horsley, *Recommended Practice for Glass Fiber Reinforced Concrete Panels*, 4th Edition, Precast/Prestressed Concrete Institute, 2001.
8. *Innovation by Design: Glass Fiber Reinforced Concrete Cladding*, Publication GFRC-3-01, Precast/Prestressed Concrete Institute, 1993.
9. K. Ohtomo, T. Yoshimura, H. Fujii, *Alkali-Resistant Glass Compositions and Alkali Resistant Glass Fibers Prepared Therefrom*, U.S. Patent 4,140,533, 1977, assigned to Kanebo Ltd. (JP) and Nippon Electric Glass Company Ltd. (JP).
10. C.D. Johnston, "Glass Fiber-Reinforced Cements and Concretes," Chapter 6, *Properties and Applications—Fiber-Reinforced Cements*, Gordon & Breach Sci. Pub., 2001.
11. S. Diamond, "The GFRP Durability Problem: Nature, Characteristics, and Test Methods," pp. 199-209 in *Proceedings of the Durability of Glass Fiber Reinforced Concrete Symposium*, Prestressed Concrete Institute, November 12-15, 1985.
12. D.E. Day, *Iron Phosphate Compositions for Containment of Hazardous Metal Waste*, U.S. Patent 5,750,824, 1996, assigned to the University of Missouri.
13. B. Tansel, B. Reyes-Osorno, I.N. Tansel, "Comparative Analysis of Fluorescent Lamp Recycling and Disposal Options," *J. Solid Waste Technol. Mgmt.*, **25**[2] 82-88 (1998).
14. S.T. Reis, D.L.A. Faria, J.R. Martinelli, W.M. Pontuschka, D.E. Day, C. S.M. Partini, "Structural Features of Lead Iron Phosphate Glasses," *J. Non-Cryst. Solids*, **304**, 189-195 (2002).
15. S.T. Reis, M. Karabulut, D.E. Day, "Structural Features and Properties of Lead Iron Phosphate Nuclear Wasteforms," *J. Nuclear Mat.*, **304**, 87-95 (2002)
16. ASTM C-693, *Standard Test Method for Density of Glass by Buoyancy*.
17. ASTM C-623, *Test Method for Young's Modulus, Shear Modulus, and Poisson's Ratio for Glass and Glass-Ceramics by Resonance*.
18. R.K. Brow, N.P. Lower, and C.R. Kurkjian, "Two-Point Bend Test Provides New Insight to Fiber Strength Quality," *Am. Ceram. Soc. Bull.*, **84**[10] 50-53 (2005).
19. A.J. Majumdar, J.F. Ryder, "Glass Fiber Reinforcement of Cement Products," *Glass Technol.*, **9**[3] 78-84 (1968).
20. T. Tanaka, M. Sugiyama, T. Futagami, S. Yamamoto, *A Novel Non-Alkali Glass Fiber with High Acid and Alkali Resistance*, NEG Technical Report, 2005.
21. M. Karabulut, G.K. Marasinghe, C.S. Ray, D.E. Day, O. Ozturk, G.D. Waddill, "X-Ray Photoelectron and Mössbauer Spectroscopic Studies of Iron Phosphate Glasses Containing U, Cs and Bi," *J. Non-Cryst. Solids*, **249**, 106-116 (1999).
22. G.K. Marasinghe, M. Karabulut, C.S. Ray, D.E. Day, "Structural Features of Iron Phosphate Glasses," *J. Non-Cryst. Solids*, **222** 144-152 (1997).

23. G.K. Marasinghe, M. Karabulut, C.S. Ray, D.E. Day, "Properties and Structure of Vitrified Iron Phosphate Nuclear Wasteforms," *J. Non-Cryst. Solids*, **263 & 264** 146-154 (2000).
24. ASTM C-965, *Standard Practice for Measuring Viscosity of Glass above the Softening Point*.
25. ASTM C-829, *Standard Test Method for Measurement of Liquidus Temperature of Glass by the Gradient Furnace Method*.
26. A. Kuçuk, Structure and the Physicochemical Properties of Glasses and Glass Melts, Ph.D. Thesis, Ceramics, Alfred University, Feb. 1999.
27. M. Paganelli, "Measuring Surface Tension of Glass," *Am. Ceram. Soc. Bull.*, **82**[9], 9201-9204 (2003).
28. S. Toyoda, S. Fujino, K. Morinaga, "Density, Viscosity, and Surface Tension of 50RO-50P2O5 (R: Mg, Ca, Sr, Ba, and Zn) Glass Melts," *J. Non-Cryst. Solids*, **321**, 169-174 (2003).
29. ASTM C-1557, *Tensile Strength and Young's Modulus of Fibers*.
30. ASTM C-947, *Standard Test Method for Flexural Properties of Thin-Section Glass-Fiber-Reinforced Concrete (Using Simple Beam with Third-Point Loading)*.
31. ASTM C-1228, *Standard Practice for Preparing Coupons for Flexural and Washout Tests on Glass Fiber Reinforced Concrete*.
32. D. Zhu, C-W. Kim, D.E. Day, "Corrosion Behavior of Inconel 690 and 693 in an Iron Phosphate Melt," *J. Nuclear Mat.*, **336**, 47-53 (2005).
33. Nickel aluminides: www.ornl.gov/info/ornlreview/rev28-4/text/nickel.htm
34. K.T. Imrich, K.M. Marshall, A.R. Jurgesen, J.W. Congdon, *High-Temperature Corrosion Study for RPP Low Activity Waste Melter*, Technical Report WSRC-TR-2002-00588, Rev.0, April 2003.
35. T.P. Seward, T. Vascott (Editors), *High Temperature Glass Melt Property Database for Process Modeling*, Wiley, 2005.
36. ASTM D-2584: Ignition Loss of Cured Reinforced Resins.
37. K.L. Loewenstein, *The Manufacturing Technology of Continuous Glass Fibers*, 3rd revised ed., Elsevier, 1993
38. J. Shi, "Properties of Alkaline Resistant Calcium Iron Phosphate Glasses," M.Sc. Thesis in Ceramic Engineering, University of Missouri-Rolla, August 2007.
39. E.J. Griffith, *Phosphate Fibers*, Plenum Press, N.Y., 1995.
40. D.E. Day, C.S. Ray, C-W. Kim, Iron Phosphate Glasses: An Alternative for Vitrifying Certain Nuclear Wastes, UMR, Final Report, DOE Environmental Management Science Program, December 2004.
41. M.A. Mogus, B. Pivac, K. Furic, D.E. Day, "Structural Study of Iron Phosphate Glasses," *Phys., Chem., Glasses*, **38**[2] 74-78 (1997).
42. Y.B. Peng, D.E. Day, "High Thermal Expansion Phosphate Glasses, Parts 1 and 2," *Glass Technol.*, **32**[5] 166-173 (1991).
43. Phosphate Glasses for Photonics at ONRL: <http://ornl.gov/info/ornlreview/rev27-3/text/phoside2.htm>
44. Hoya U-340 Glass for Ultraviolet Transmitting and Visible Absorbing Filters: http://www.uqgoptics.com/materials_filters_hoya/uvTransmitting_UV340.asp
45. J. Vogel, W. Holand, W. Vogel, Phosphate Glass Ceramic for Biological and Medical Applications, U.S. Patent 4,698,318, 1987, assigned to VEB Jenaer Glaswerk.
46. D.E. Day, M. Erbe, M. Richard, J.A. Wojcik, Bioactive Materials, U.S. Patent 6,709,744 B1, 2004, assigned to the University of Missouri.
47. Y.B. Peng, J.B. Koen, Bioabsorbable Glass Fiber/Polymer Composites, MO-SCI Corp., Public Health Service SBIR Phase I and Phase II programs, Grant No. 2 R44 DE08877-03, Final Report, 6/30/93.