Evaluation of geopolymer concrete for repair of rocket test facility flame deflectors

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ABSTRACT: A joint research effort by Louisiana Tech University (LTU) and NASA Stennis Space Center (SSC) was established to develop refractory geopolymer concrete. In preliminary tests, geopolymer was used to complete small repairs of the floors and walls of the refractory-lined flame trench at the SSC E-1 Cell 3 rocket engine testing facility. These repairs were then exposed to high temperature exhaust plumes of a 1780 kN class LOX/RP-1 engine. Subsequently, a controlled study was conducted of the geopolymer's performance under direct rocket plume impingement conditions. The NASA-SSC Diagnostic Test Facility (DTF) thruster, which is a 5.78 kN LOX/GH2 rocket engine, was used to generate the necessary supersonic plume environments to produce direct impingement on refractory test panels 30 cm wide x 60 cm long x 15 cm deep. Various geopolymer and commercial grade formulations were tested. Data collected included surface profiles of the test panels giving localized erosion rates during the test.

1 INTRODUCTION

Geopolymer Concrete (GPC) is an emerging class of cementitious material, which offers a sustainable, low energy consuming, low carbon footprint, 100% substitute to Portland cement as a cementitious binder in construction applications (Davidovits, 2005). Geopolymer research at Louisiana Tech University is directed towards converting locally available Class F fly ash into a high performance refractory material that can be used as a monolithic refractory for applications under extreme conditions of temperature and pressure.

The term “geopolymers” refers to a 3D polymeric network of alumino-silicate binders. The polymerization process involves a rapid reaction of silico-aluminate minerals in the source material with the alkali metal hydroxide/silicate activator solution. The outcome of the polymerization reaction is a 3D polymeric chain/network structure of Si-O-Al-O bonds. (Davidovits, 1991). Due to the absence of water in the geopolymer molecule, these binders are capable of maintaining thermal stability at temperatures up to 1000°C without a significant change in their structure (Barbosa & MacKenzie, 2003).

The fly ash source is of extreme importance for the fire performance of the resulting geopolymer, which tends to remain amorphous after high temperature exposure (Rickard *et al*, 2012). However, some authors (Duxson & Lukey, 2007) have found crystallization at temperatures as low as 600°C, which suggests that the highly variable composition of geopolymer raw materials, especially fly ash, has a high impact on the type of crystallization. Heating and cooling conditions also play a role in this matter. Duxon also found that the choice of alkali is also of significant importance for thermal expansion. Unlike conventional refractories, some geopolymers have been found to have increased compressive strength after being exposed to elevated temperature (Kong, *et al*, 2007). This is especially important when comparing with Portland cement, which is highly susceptible to fire (Sanjayan & Stocks, 1993).

The development of robust monolithic refractory materials with improved physical properties for aerospace applications is directly in line with the missions of NASA. The application of a high performance refractory material to rocket engine flame deflectors will significantly improve support infrastructure at NASA launch and rocket propulsion test facilities.

The current paper describes the development and testing of a high temperature performance refractory geopolymer concrete that was performed at NASA

Stennis. Geopolymer concrete was placed in the NASA-SSC E1 test stand and exposed to large-scale rocket exhaust plumes. Additionally, geopolymer concrete panels were tested during a 2-week comprehensive program, where the NASA-SSC Diagnostic Test Facility (DTF) thruster was used to generate supersonic plume environments on a 30 cm wide x 60 cm long x 15 cm deep refractory panels. The DTF operates on LOX/GH2 propellants producing a nominal thrust of 5.78 kN. The DTF operating conditions and facility configuration were selected to produce heating rates that were of the same magnitude as that of the full-scale engine tests.

2 LABORATORY TESTS

2.1 *Raw materials*

Fly ash from CLECO's Dolet Hills Power Station was used due to its proximity to the SSC and its high quality and consistency. The chemical and phase composition and other characteristics of the fly ash are summarized in Table 1.

Table 1. Fly ash characteristics.

Oxide	% wt.	Phase	%wt.
SiO_2	59.32	Quartz	12.2
Al_2O_3	19.72	Mullite	4.8
CaO	6.90	Amorphous	83.0
Fe_2O_3	7.22	(% > 45 μm)	62.97
MgO	2.23	Specific gravity	2.23
SO_3	0.36		
Na_2O	1.11		
K_2O	1.27		
TiO_2	1.00		
Moisture	0.08		
LOI	0.15		

For the activation, a liquid silicate with a SiO_2/Na_2O ratio of 3.22 in a 37.2 weight percent solution in water and a viscosity of 180 centipoises was utilized. Sodium hydroxide in pellets was used to obtain the desired Na:Al ratios in the final geopolymer. Table 2 summarizes the types of aggregate used for this project.

2.2 *Geopolymer formulation*

The reactive components of the fly ash were calculated based on its amorphous component. Then, an activation system was formulated to yield a Si:Al ratio between 2 and 3. A Na:Al ratio between 1 and 2.5 was kept throughout the experimentation.

Table 2. Aggregate used to produce geopolymer concrete.

Aggregate type	Mullite-based	Alumina-based
Chemical composition	50% SiO_2, 46% Al_2O_3	99.7% Al_2O_3
Phase composition	65% Mullite, 20% Glass, 15% Cristobalite	99.7% Corundum
Specific gravity	2.6	3.7
Water absorption	3.6%	1.65%
Melting point	1650°C	2000°C

2.3 *Test results*

Mechanical and thermal tests were conducted at Louisiana Tech to evaluate the quality of the geopolymer concrete.

Mass loss laboratory tests were conducted at Louisiana Tech University to evaluate the performance of geopolymer under flame exposure. A torch flame of 1300°C was directed at geopolymer cubes produced with Tabular Alumina and M47. The setup of the torch can be seen in Figure 1. Mass loss was evaluated for different geopolymer concrete formulations and it is shown in Table 3.

Figure 1. Geopolymer cube exposed to a flame of 1300°C.

3 PRELIMINARY EVALUATION OF GEOPOLYMER AT THE E-1 CELL 3 TEST STAND

Information from computational modeling, laboratory testing, and concrete guideline ACI 211.1 was incorporated in Louisiana Tech's geopolymer mix design software to create a formulation to be tested at NASA-SSC Test Facility (E-1 Cell 3). This formulation was installed on a panel of dimensions 30 cm.-15 cm. horizontal x 120 cm.-0 cm. up slope x 120ft. thick = 56.53 lt. on top of the trench and an additional 10 cm x 10 cm x 10 cm. patch on the lower right hand side part of the trench (Figure 2). The slab was cured using a heating blanket for 24 hours. A smaller second patch was also casted with a slightly modified geopolymer formulation.

Table 3. Summary of mass loss results after flame tests.

Formulation	Mass loss (%)
Geopolymer Paste	2.56
Geopolymer Coating	1.70
Geopolymer with Alumina Aggregate	0.70
Geopolymer with Mullite Aggregate	1.45
Geopolymer with Tabular Alumina Ambient Cured	1.22

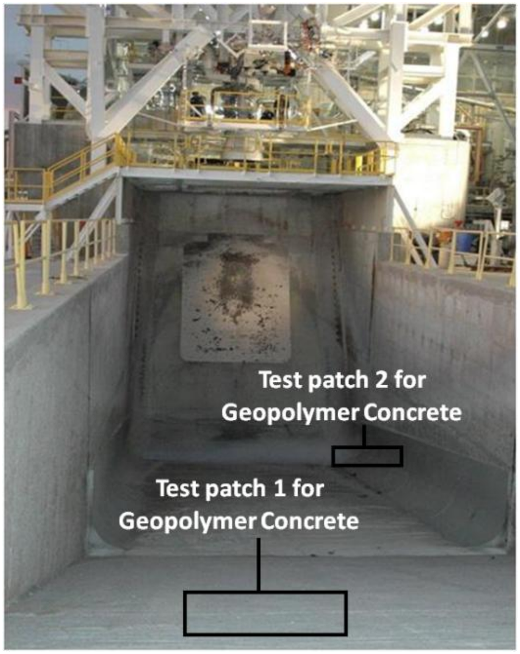


Figure 2. Location of the first two geopolymer repair sections at E-1 Cell 3.

The geopolymer sections of the flame trench were examined after a nominal rocket engine test which lasted approximately 55 seconds producing temperatures as high as 2200°C. The appearance of both sections after the test is shown in Figure 3.

Figure 3.Geopolymer sections after rocket engine test.

The geopolymer material was observed to erode/ablade at nearly identical rates as the surrounding commercial grade refractory material. There was no large-scale loss of geopolymer material and no indication of de-bonding of the geopolymer from the surrounding refractory of the concrete substrate. The geopolymer material has since undergone exposure to numerous subsequent engine tests with continued excellent performance.

4 DIRECT PLUME IMPINGEMENT TESTING OF GEOPOLYMER

4.1 *Test setup*

The NASA Stennis Diagnostics Testbed Facility (DTF) rocket engine was used in this study. The DTF engine is a 5.78 kN gaseous-hydrogen/liquid-oxygen rocket engine that has been designed to produce plume properties (temperature and pressure at first mach diamond) that are very similar to the SSME (Tejwani et al, 1992). A schematic of the engine is given in Figure 4. Typical operating conditions of the engine are a chamber pressure of 3.45 MPa (relative to vacuum) and mixture ratio (O/F) of 5.0. For the current project, the chamber pressure was increased to approximately 4.33 MPa and O/F of 3.8, where the LOX and GH2 flow rates were on average 1 and 0.26 kg/sec respectively. The DTF engine was fitted with a bell nozzle that had an exit-to-throat area ratio of 6.15. These conditions were selected to produce dynamically similar data for the larger scale E-1 Cell 3 facility. Table 4 is a summary of the DTF nominal operating conditions and estimated plume properties. The plume properties are nominal predicted values obtained from the NASA Chemical Equilibrium Analysis Code (Gordon and McBride, 1994).

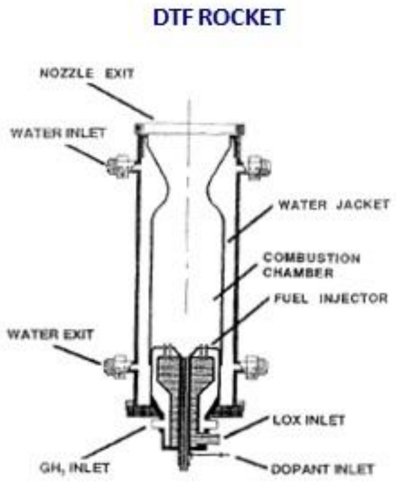


Figure 4. Schematic of the DTF Rocket Engine

Test durations were limited to prevent excessive erosion of the test panels and subsequent plume detachment. A cumulative series of short duration (5 seconds) tests were conducted for each panel until a 55 second total duration was achieved or the plume became too severely detached. Single long duration tests lasting up to 55 seconds were also planned to verify if the data was independent of test duration (i.e. thermal equilibrium is reached). Engine parameters and estimations of nozzle exit conditions can be seen in Table 4.

Table 4. Nominal DTF Engine Parameters and Corresponding Estimations of Nozzle Exit Conditions

Engine Parameters		
D_{NE}	Nozzle Exit Diameter	7.4 cm
AR_{NE}	Area Ratio of Diverging Nozzle	6.15
P_o	Combustion Chamber Pressure	4.3 MPa
O/F	Combustion Chamber Oxygen-to-Fuel Ratio	3.8
Nozzle Exit Conditions		
P_{NE}	Nozzle Exit Pressure	0.095 MPa
T_{NE}	Nozzle Exit Temperature	1234.4°C
M_{NE}	Nozzle Exit Mach Number	2.98
MW_{NE}	Nozzle Exit Molecular Weight	9.676
γ_{NE}	Nozzle Exit Ideal Gas Ratio of Specific Heats	1.27

4.2 *Test panel configuration*

A steel structure was designed to support ablative refractory panels under direct plume impingement by the DTF engine. The panels were oriented at an angle (θ) of 30 degrees off plume axis as depicted in Figure 5. A 30-degree impingement angle was selected as most static test stands at NASA have such angles so as to produce a turning of the plume with an oblique shock. If the plume were to be deflected at a more aggressive angle (e.g. 75 degrees), a normal shock would form producing excessive heating and reverse flow up the deflector wall. By maintaining a consistent deflector angle, the flow profile over the subscale ablative panels would be dynamically similar to that of a full scale facility. In addition to deflector angle, the separation distance of the engine from the deflector panel was important as it would affect the level of heating to the test panels. In all tests, the engine was positioned such that the nozzle exit plane was an axial distance of 20.3 cm (or 2.74 DTF nozzle-exit diameters) away from the test panels. This distance was selected based on an a-priori knowledge that this would place the deflector panel just downstream of the first Mach disk in the plume. As such, the heating rate to the deflector would be maximized. The impingement pressure and heating rates for this test configuration were estimated using computational fluid dynamics (CFD) modeling.

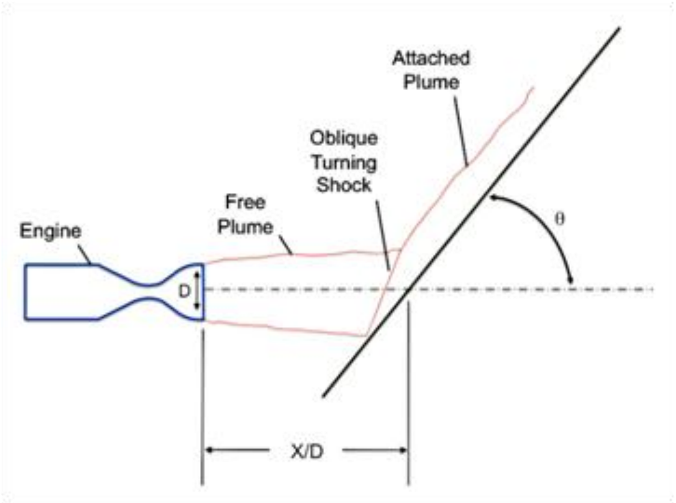


Figure 5. Engine-Deflector Geometry and Orientation

Each test panel was 60 cm long by 30 cm wide by 10 or 15 cm thick, where the length of the test panel was oriented in-line with the primary flow direction of the impinged gases. The width and length of the test panels were selected to be sufficiently large to allow the entire plume to impinge on the panel. Also, it was critical for obtaining accurate erosion data that the deflector was a sufficient size such that the primary impingement zone would not be influenced by the test panel dimensions. The refractory panel materials tested will be discussed in the next section.

The refractory test panels were evaluated by first performing a cumulative series of tests where each test consisted of a 5 second steady burn of the engine. The same test panel was then used during successive 5 second tests. Before and after each test, the surface profiles of the deflector panels were measured using a specially designed depth measuring gauge with an accuracy of +/- 0.0254 cm. The surface profiles were measured across the panels on a 2.54 cm by 2.54 cm grid. Once the preliminary evaluation was completed, a single long duration test lasting up to 55 seconds was conducted using a new panel to obtain near steady-state erosion rate data (i.e. thermal equilibrium is reached). A 10 or 15 cm thickness for the test panel material was selected to avoid erosion thru the test panels during the maximum expected test duration. Total cumulative test durations were limited to prevent excessive erosion of the test panels and subsequent plume detachment (Figure 6).

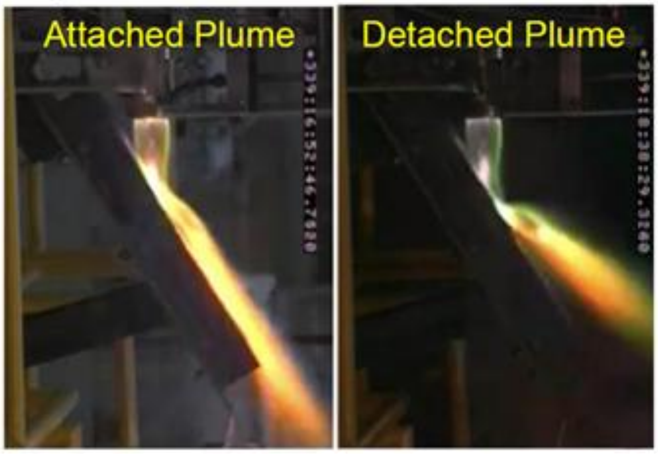


Figure 6. Example of Plume Detachment after Excessive Panel Erosion

4.3 *Test panel preparation*

All geopolymer test panels were prepared at the Geopolymer Laboratory at the Trenchless Technology Center of Louisiana Tech University. The concrete mix design for all of the samples was obtained using custom-developed software, developed at Louisiana Tech. The software utilizes user input such as raw materials' chemical composition, density, and absorption, together with the desirable properties of the application at hand to produce an initial geopolymer mix design. The initial mix design was then prepared in the laboratory and optimized as necessary.

Several samples of geopolymer concrete, mortar, and other commercial refractories were also repaired with geopolymer mortar (GPM) after the first plume test to evaluate adhesion to the parent material and reparability in general. Additionally, two samples had thermocouples installed with the intention of monitoring the heat evolution in the sample as the tests were being conducted. Two panels were manufactured for each geopolymer formulation. The control variables include type of refractory aggregates (Tabular Alumina, Mulcoa 70 and Mulcoa 47) and the grade of geopolymer product (concrete or trowable mortar). All the samples were subjected to standard geopolymer curing (60°C for 24 hours) with the exception of two specimens that were ambient cured for 28 days before testing.

Table 5 shows the samples that were tested during the two week program. Two repetitions (A, B) were used for each sample. In general, the samples were subjected to incremental 5-5-5-15-30 second flame exposure durations and to a 15 or 30 accumulated exposure, depending on the sample performance (e.g., if the plume became detached). The testing matrix shown below was developed to enable systematic evaluation of the performance of various formulations and grades of geopolymer as well as commercially available refractory products currently utilized by NASA SSC.

Table 5. Refractory Panel Designation and Description

Test Panels Using Geopolymer	
GPM	Geopolymer mortar (trowable) with Tabular Alumina
GPC1	Geopolymer concrete grade 1 (Tabular Alumina)
GPC2	Geopolymer concrete grade 2 (Mulcoa 70)
GPC3	Geopolymer concrete grade 3 (Mulcoa 47)
UGPC1	Ambient cured GPC1
Test Panels Repaired with Geopolymer	
RGPM	GPM panel repaired with a new layer of GPM
RGPC	GPC1 panel repaired with GPM
RSEN	Sentinel RC panel repaired with GPM

An attempt was made to measure the temperature profile of the geopolymer panels using embedded thermocouples. Ultimately, this proved to be unsuccessful. Most of the thermocouples melted before producing useful results, while others reached their upper range limit, which was below the actual temperature generated at the impingement zone. Future tests will incorporate thermocouples with higher temperature ranges.

5 RESULTS

Each refractory test panel was subjected to direct plume impingement from the DTF engine. The hot exhaust gases from the DTF engine impinged on the test panels at supersonic speeds, producing a complex pattern of intense shock induced heating and pressure loading as depicted in Figure 7. Figure 7 are results from NASA-SSC computational fluid dynamic (CFD) simulations of the plume induced loading on the 30 cm x 60 cm panel. The position of the DTF engine is also shown in the figures for reference. Due to 30-degree impingement angle of the plume to the panel (characteristic of rocket plume deflectors), the high heat-flux zone is elliptical in shape with maximum expected erosion in the downstream end of this elliptical impingement zone. This shape and distribution was confirmed for all test panels.

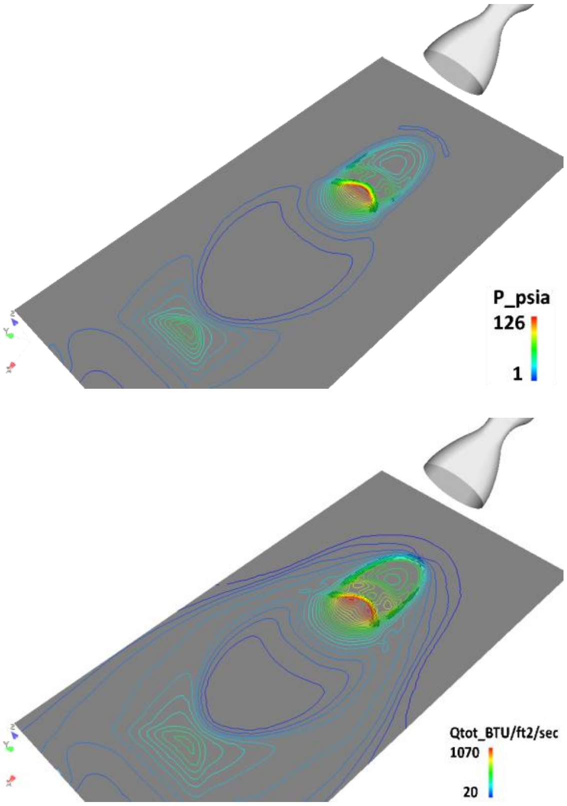


Figure 7. Predicted Deflector Panel Contours of Pressure (top) and Cold Wall Heat Flux (bottom)

One of the critical parameters for a refractory-lined rocket deflector is the rate at which the materials will ablate/erode during a rocket test or launch. Based on previous testing of commercial grade refractories in this environment, it was of interest to obtain the erosion rate data for multiple short (5 seconds each) tests on the same panel and for single long (15 second) duration tests. This classification of data would provide an understanding as to the material's sensitivity to transient thermal loads versus conditions where thermal equilibrium was reached in the heat-affected zone of the panel.

Comparing the maximum erosion (due to ablation and mechanical shearing) that was generated on each test panel provided a good overall indicator as to the relative performance of the refractory panels. Figure 8 shows the maximum erosion for all geopolymer formulations in comparison with some of the commercial refractories previously investigated by NASA. The data is for a single 5-second rocket firing on each panel. Under these short, transient conditions, all geopolymer formulations exhibited lower total erosion depths in comparison to the selected commercially available refractories. The data also indicated a relatively small sensitivity of the geopolymer ablative performance to the geopolymer formulations, namely GPC1-3 and GPM. The numeral values 1, 2 and 3 stand for aggregates with different refractory performance, with (1) being the material with higher chemical purity and (3) the material with lowest chemical purity. The GPM is a geopolymer mortar formulation. The letter "U" stands for ambient cured (other specimens were forced cured). Using the data from these tests, a cost-study could be performed to examine the most cost-effect approach for a particular application. These tests were also aimed at determining if the performance of the ambient cured grade geopolymer specimens matched that of their forced cured counterparts. Comparing UGPC1 to GPC1 showed only a small benefit in non-ambient curing of the material. This translates into significant savings in the installation costs of large-scale rocket deflectors.

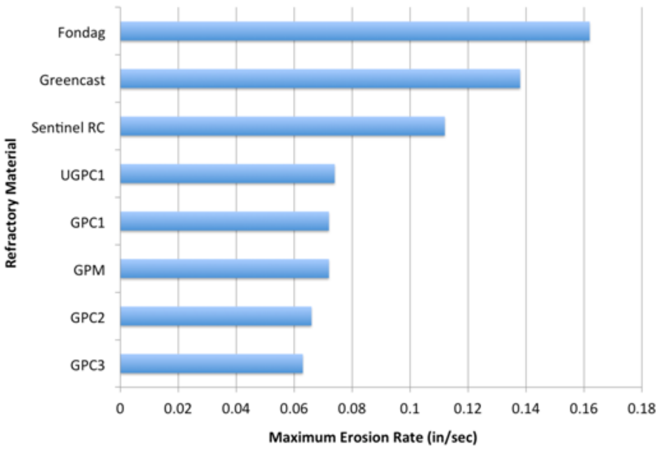


Figure 8. Maximum erosion rates when subjected to a 5-second DTF rocket firing.

While the above results provide an initial indication of the performance of the geopolymer materials, it does not provide any guidance on whether the material will continue to provide the same performance due to subsequence short firings or long-duration firings. Figure 9 shows the cumulative effect of rocket firings on the maximum erosion rates. Excluding GPC3, all the other geopolymer formulations showed the same general trend in the maximum erosion rate with cumulative testing. Specifically, a near linear decrease in maximum erosion rate was observed as the overall exposure of the test panels to the rocket plume was increased. It is hypothesized that this behavior could be due to two factors: (1) the material was improving its resistance to erosion due to heat treatment or (2) the maximum heat rate was decreasing due to surface changes of the eroding test panel. In either case, the relative performance of each geopolymer formulation remained consistent over all cumulative testing. Namely, GPC3 showed the best performance while the ambient cured UGPC1 exhibited the poorest performance of the geopolymers. However, the UGPC1 performance is still quite competitive compared to commercial grade refractories as will be discussed in the next section.

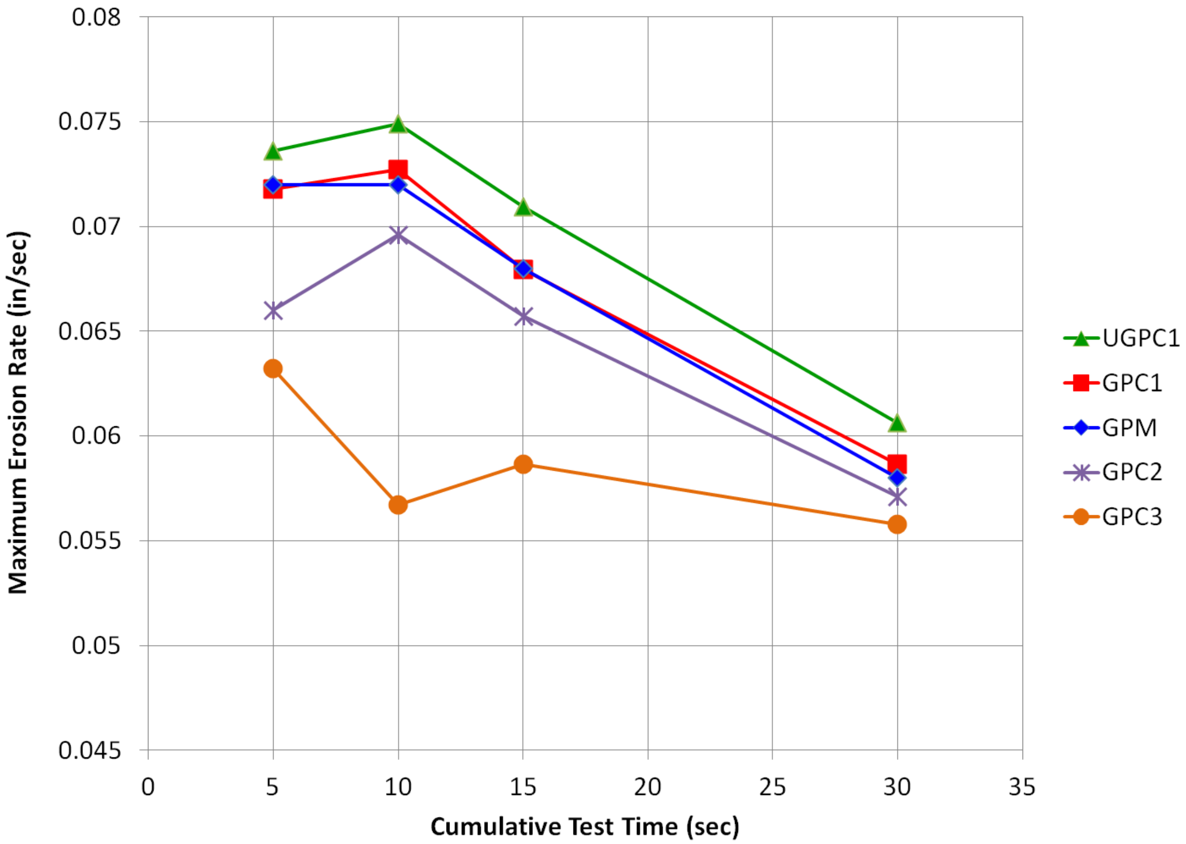


Figure 9. Geopolymer maximum erosion rates due to successive DTF rocket firings.

In most rocket engine test programs, the duration of the hot fire will not be of the order of a few seconds, but rather could occur over a significant period of time (minutes or even hours). Thus, it is critical that the material be able to withstand the thermal and shear loading of the rocket exhaust under long duration testing, i.e. where the material has reached some “steady-state” erosion behavior. To obtain this data, new refractory panels were fired upon for at least 15 seconds continuously. This provided enough time for a steady-state condition to be reached but not long enough to cause substantial erosion of the panel surface and thereby greatly affect the heating patterns. Figure 10 provides a direct comparison of all the geopolymer formulations to commercial grade refractories tested at NASA-SSC during this test program as well as earlier programs under similar conditions. The data shows that all geopolymer materials performed very well under these “steady-state” conditions. Their resistance to erosion by the rocket plume was greater than or comparable to the commercial grade refractory materials. This included the ambient cured geopolymer formulation UGPC1. Figure 11 is an example of the profiling images that were obtained after erosion measurements were taken.

Other tests were also conducted during the two-week program, including repaired geopolymer and Sentinel RC panels (Figure 12). All the panels were repaired with geopolymer mortar (GPM). One of the repaired Sentinel panels included an anchor to simulate the anchoring that takes place when repairing the NASA-SSC E-1 rocket flame deflector. Results showed that the adhesion of geopolymer to the parent surfaces was sufficient to withstand all the loads produced by direct rocket plume impingement, and that the use of mechanical anchors did not cause any adverse effects. Specifically, the repaired panel behaved in a manner similar to the monolithic unit in spite of the fact the stainless steel anchor thermally ablated along with the Geopolymer material.

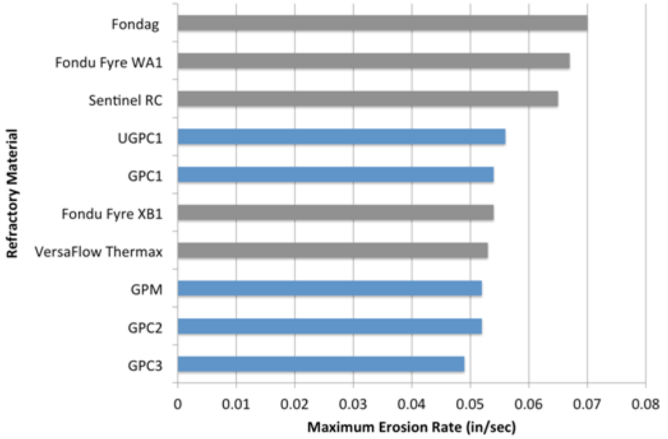
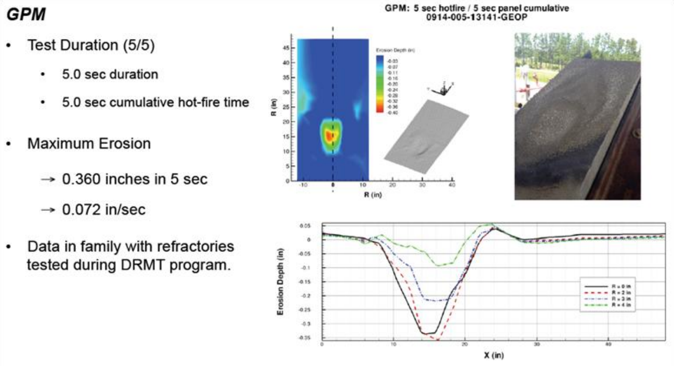


Figure 10. Maximum erosion rates after a single 15 second DTF rocket firing – geopolymer (branded "GP") and commercial products.


GPM

- Test Duration (5/5)
  - 5.0 sec duration
  - 5.0 sec cumulative hot-fire time
- Maximum Erosion
  - → 0.360 inches in 5 sec
  - → 0.072 in/sec
- Data in family with refractories tested during DRMT program.

Figure 11. Profile of a GPM panel after the 5 second test.

6 CONCLUSIONS

The current testing program showed that the LTU geopolymer products had an equivalent or in some cases superior resistance to rocket plume erosion compared to commercial refractories currently being tested by NASA Stennis Space Center.

Preliminary testing at Louisiana Tech demonstrated the geopolymer's ability to withstand thermal shock and exposure to flame. A computational model was created to find the optimal chemical ratios for geopolymer to be exposed to elevated temperatures. This information was incorporated in the geopolymer software to produce mix designs for field applications and panel construction.

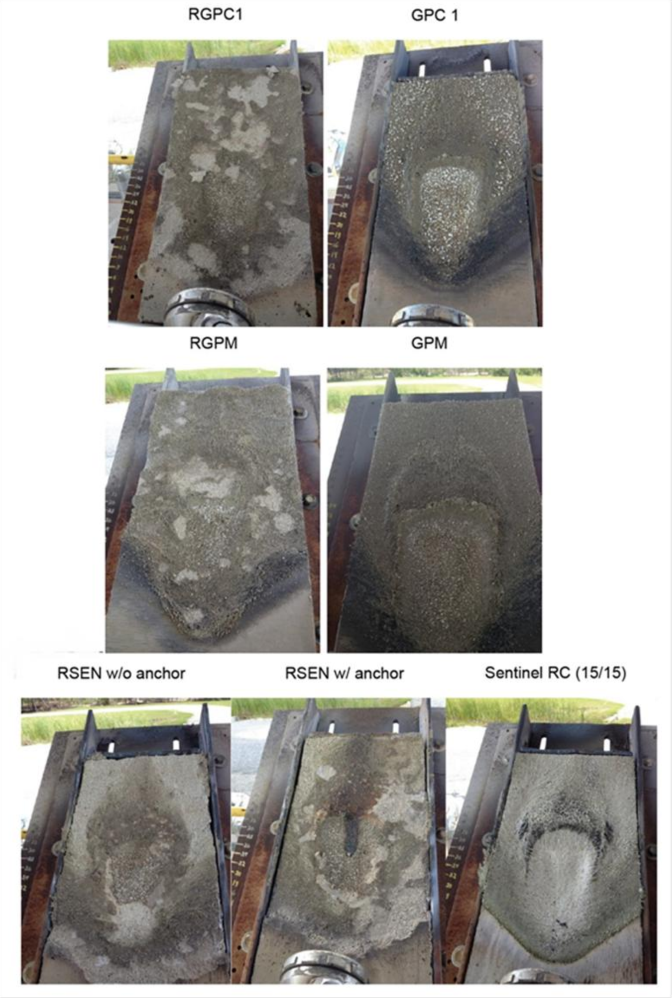


Figure 12. Repaired GPC1 panel (after 15/15 test) and original GPC1 panel (after 30/30 test). Repaired GPM with GPM panel (after 15/15) and original GPM panel (after 15/15) (middle). Repaired Sentinel panel without anchor after 15/15 test (bottom left), repaired Sentinel panel with anchor after 15/15 test (bottom middle) and original Sentinel panel after 15/15 test (bottom right).

Field testing at NASA Stennis demonstrated geopolymer's ability to withstand full-scale 55 second rocket engine testing in different sections of the flame trench.

Systematic testing of the geopolymer panels revealed erosion rates were lower in the majority of cases in comparison to commercial refractories for tests of the same duration. Geopolymer also proved to be a good candidate for the repair of existing commercial refractories due to its excellent adhesion to parent surfaces.

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