Geopolymer Refractory System for Molten Salt Thermal Storage Tanks

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Molten Nitrate and/or Chloride Salts are common candidates used to store the thermal energy associated with solar thermal energy applications. These molten salts must be contained and managed in a storage system, usually consisting of a hot and cold tank. The stored thermal energy is recovered from the molten salt as it passes through a heat exchanger and a power generator when direct sunshine is unavailable. The problem lies with the tank lining. For example, special stainless-steel tanks have been used for molten nitrate salts. Still, stainless steel's corrosion and thermomechanical failure at the salt operating temperature is a major concern. Over time the stainless steel corrodes and degrades, so there is a need for a refractory system that is non-reactive to the molten salt but at the same time is an efficient thermal insulator, especially when salt permeation into the tank liner could occur. With a reduced tank shell temperature, more affordable tank construction materials such as carbon steel can be used. A Geopolymer (GP) binder system was determined to fit this bill when loaded with fly ash microspheres. The composition and properties of this GP refractory will be presented in detail. Still, a refractory with a nominal density of 60 lbs./ft3 (0.96 g/cc), compressive strength of > 2000 psi (13.8 MPa) and a Thermal Conductivity ranging from 2.2 to 2.8 BTU-in/hr-ft²·°F (depending on the Mean Temperature) with a use limit of 1832°F (1000°C) was developed.

Background

The objective of this project was to provide a more reliable and cost-effective internal thermal solution to current and future-generation Concentrating Solar Power (CSP) with Thermal Energy Storage (TES) tanks that use molten salts as the Heat Transfer Fluid (HTF) and storage media. The aim was to engineer a composite, ceramic-based geopolymer insulation material that possesses thermal insulation properties without significantly sacrificing resistance to salt permeation and mechanical strength. This is the major tradeoff in traditional ceramic insulation design.

Conceptual Tank Insulation Design

Figure 1 shows the conceptual design of the tank wall's internal insulation and presents a few key considerations for the geopolymer insulation layer.

- The geopolymer layer will be partly saturated by the molten salt where the thermal conductivity is expected to be around 0.45 W/m K. The rest of the geopolymer layer, "Dry GP buffer," will be dry with a lower thermal conductivity around 0.30–0.35 W/m K. The dry GP is designed to stay below the salt freeze temperature and serves as a buffer zone in case the heat transfer of the wall changes and the molten salt/solid salt interface (the yellow dashed line) moves. The molten salt/solid salt interface is the most important feature of the design because the frozen solid salt effectively self-contains the molten salt. If there is enough physical space and temperature drop for the molten salt to freeze in the buffer region, molten salt will always be contained, and the containment will "self-heal" if a crack develops inside the solid salt region. Equally important, the buffer zone is there to prevent molten salt from permeating into the highly insulating yet fragile "other internal insulation" layer.

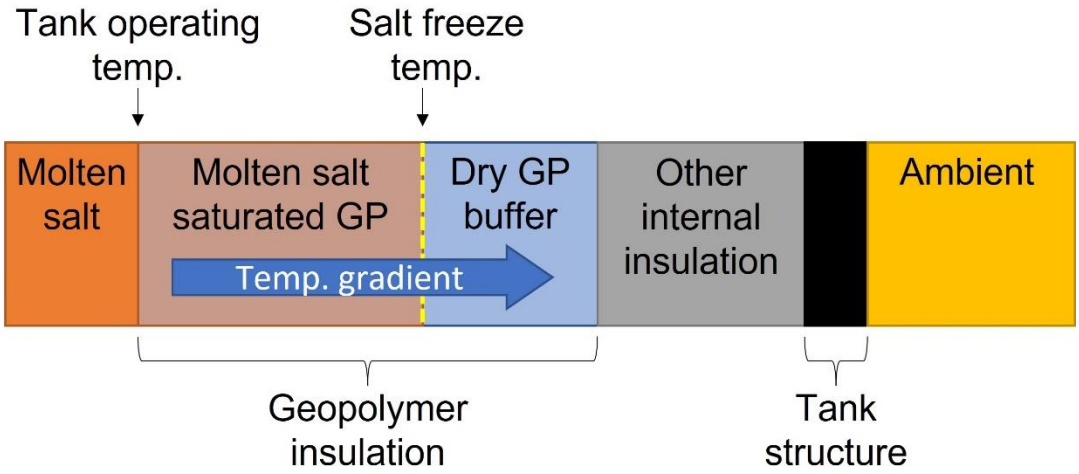
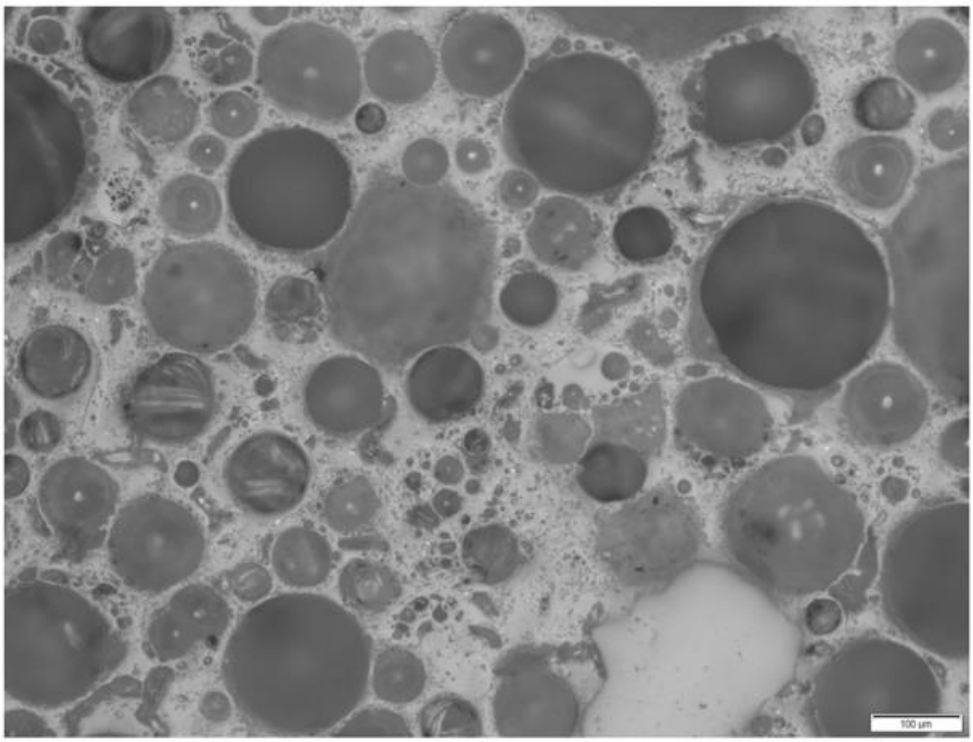


Figure 1. Schematic of the tank wall insulation design. The yellow dashed line indicates the molten salt/solid salt interface.

- Around the molten salt/solid salt interface, there will be stresses associated with the volume change between the molten and solid salts. For the nitrate salts used by current generation CSP and TES, the volume change is about 4.6% [1]; for the chloride salts as one HTF and storage candidates by next generation CSP, the volume change is estimated to be about 20% [2]. This could raise concerns over the mechanical strength of the geopolymer around the interface especially when the interface moves back and forth over time due to slight changes of heat transfer.
- The entire geopolymer insulation layer will be under thermal stresses due to the temperature gradient of the TES tank (estimated to be around 200–500 °C/m).
- The molten-salt-saturated section of the geopolymer needs to maintain most of its closed porosities (e.g., formed by incorporation of Cenospheres) over time and avoids extensive chemical attack from the salt on the closed porosities. The goal is to minimize loss of thermal insulation performance due to permeation of molten salt into the closed porosities.

Figure 2 - Micrograph of the geopolymer refractory at 100x magnification is shown below:



Materials and Methods

The following materials were used in this research:

Metakaolin

Metakaolin was chosen as the aluminosilicate material due to its high purity, reactivity of its components and being more active for geopolymerization than other materials. The Metakaolin, made by calcining kaolin, was supplied by IMERYS, and was used throughout this study.

Table 1 – Chemistry and Properties of IMERYS Metakaolin

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	LOI 1000°C	LOI (400-600°C)
48.95	48.04	0.40	1.49	0.435	0.058

Sodium Silicate

K-Brand Sodium Silicate as supplied by PQ Corporation was used in this study. This Sodium Silicate, which has a high concentration of Silica, has the chemistry below:

Table 2 – Chemistry and properties of PQ Corp K-Brand Sodium Silicate

SiO_2/Na_2O	% NaO_2	% SiO_2	Be	lbs/gal	g/cc	pH	Viscosity (cp)	Consistency
2.88	11.00	31.70	47.0	12.3	1.48	11.5	960	Sticky Heavy Silicate

Fly Ash Spheres

ES500 RM3 Cenospheres, as supplied by Cenostar Corporation were used in this study. These microspheres are some of the purest available and have the properties below.

Table 3 – Chemistry and properties of ES500 RM3 Fly Ash Microspheres

% SiO_2	% Al_2O_3	% Fe_2O_3	Bulk Density (g/cc)	True Density (g/cc)	m.p. (°C)
50-60	22-30	1.5-5.0	0.32 – 0.45	<0.85-0.98 +/- 2.5%	1200-1400

Alumina/Silica LW Aggregate

The original Mulcoa 43 LW aggregate, as supplied by IMERYS was used in this study. It is acknowledged that after 75% of the study was completed, IMERYS made the decision to not offer this aggregate anymore. The original Mulcoa 43 LW aggregate was chosen because of its reported ~20% closed porosity. Although unfortunate, it is believed that other Alumina-Silica LW aggregates can be used in the GP formulations developed in this study.

Table 4 – Chemistry and properties of Mulcoa 43 LW Aggregate

% Al_2O_3	% Fe_2O_3	Alkali	Sp. Gravity (g/cc)	% Porosity
41.3	1.3	0.3	1.7	40 (1/2 closed)

Silica Fume

A-1000 Silica Fume as supplied by Technical Silica Company was used in this study. This Silica Fume was chosen because of its low impurity level.

Table 5 – Chemistry and properties of A-1000 Silica Fume

% SiO_2	% Al_2O_3	% Fe_2O_3	% Carbon	% MgO	% Na_2O	Bulk Density(g/cc)	pH	Color
90.00	1.20	0.30	0.20	0.07	0.01	0.26 to 0.40	3.5-5.0	Lt. gray

Sodium Hydroxide

NaOH beads supplied by Carolina Biological Supply Company were used in this study. This was an analytical grade sodium hydroxide with a purity of 99%. 10 Molar solutions were made with deionized water. 10M was selected because several GP technical publications stated it best for geopolymerization and strength development.

Set Accelerator

Fabutit 748 Aluminum Phosphate, as supplied by Budenheim was used in this study to accelerate the setting times of the GP compositions. This chemical is a known setting agent for Sodium Silicate compositions.

Table 6 – Chemistry and properties of Fabutit 748

Al_2O_3	P_2O_5	pH (10% Suspension)	Bulk Density (g/l)
~36	~60	~2.3	650

Sample Preparation

Several Geopolymer (GP) formulations were evaluated but mix GP-20-3 with 2.7% added water was down selected for extensive testing. The ratios below follow Davidovits recommendations for the ideal development of geopolymerization and strength:

Al/Na	1.00
Si/Na	2.50
Si/Al	2.50

The chemistry of mix GP-20-3 is as follows:

- Al_2O_3 28.5
- SiO_2 60.8
- Fe_2O_3 1.5
- TiO_2 1.2
- Na_2O 5.9
- P_2O_5 0.1

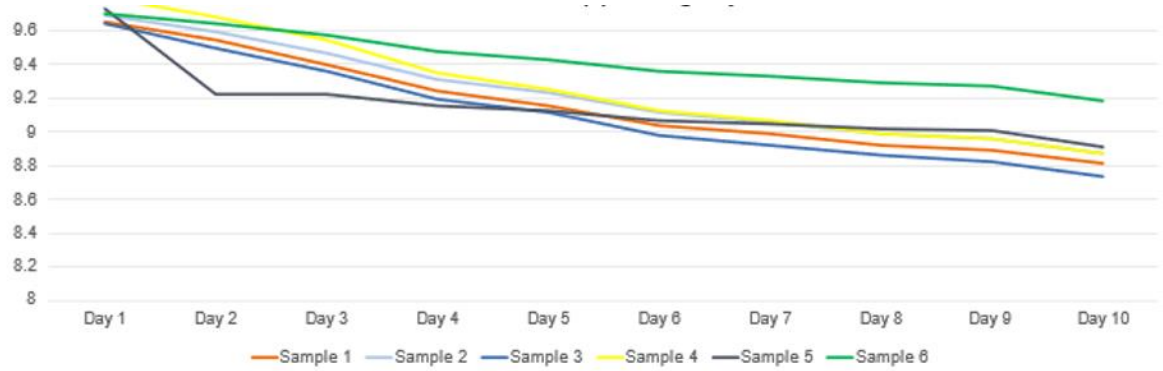
Casting Characteristics:

The casting characteristics were typical for a chemically bonded castable; like a Phosphate bonded castable. It flowed well when 2.7% water was added with external vibration but not sure it would flow well with an immersion vibrator.

Figure 3 – Sample preparation

In order to see the effectiveness of wrapping the samples in plastic, the samples were weighed every day for10 days (about 1 and a half weeks). The weight loss in these small samples stabilized after 7-days.

Figure 4 - Weight loss on GP-20-3 per day at 60C curing



Property Testing

The following property testing was done on samples mix GP-20-3w/2.7% added water:

- Density
- MOR – Modulus of Rupture
- CCS – Cold Crushing Strength
- PLC – Permanenet Linear Change
- Thermal Conductivity (Hot Wire)
- Thermal Expansion
- Porosity using Isopropal Alcohol (IPA)
- Mercury Porosity

Results

The physical property results for GP-20-3 are shown below in Table 7.

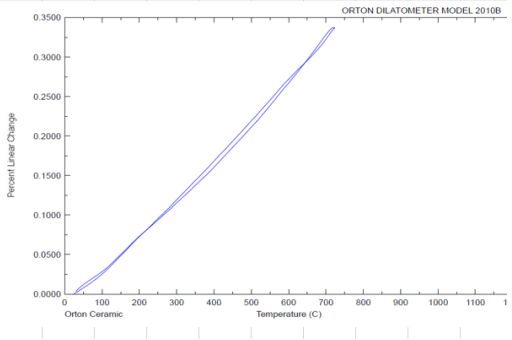
Table 7 – GP-20-3 Physical Properties

60C 7-day Density (g/cc)	400C 5hrs Density (g/cc)	400C MOR (MPa)	400C CCS (MPa)	%PLC (RT to 60C)	% PLC (RT to 400C)	IPA Porosity (60C)	IPA Porosity (400C)
0.98	0.89	2.79	17.0	-0.4	-1.0	20.1	16.3

Thermal Expansion:

Figure 5 - The Thermal Expansion (Cycle 3) on the GP-20-3 mix is shown below:

Sample:	NREL GP-20		Sample Length Before:	2.016	
Run #:	Orton - 3		Sample Length After:	2.016	
	Temperature	PLC	Coeff.(C)		Coeff.(F)
Ascending	30	0.0018	2.40E-06		1.33E-06
	720	0.3356			
Descending	720	0.3374	2.40E-06		1.33E-06
	40	0.0081			
Avg. Ascending (C)	2.40E-06	Avg. Descending (C)	2.40E-06		
Avg. Ascending (F)	1.33E-06	Avg. Descending (F)	1.33E-06		
	Grand Average (C)	2.40E-06			
	Grand Average (F)	1.33E-06			



This data is on a sample that was not saturated with molten salt. External labs were reluctant to run a sample that contained salt to avoid contaminating the dilatometers. These thermal expansion values are lower than those of most conventional castables but are certainly not as low as a castable containing fused silica.

Hot Compressive Strength Testing

A hot MOR testing unit was modified to determine the 550°C and 720°C compressive strengths of the GP-20-3 sample, both unsaturated and saturated with salt. This was done because again there was a reluctance to run samples saturated with salt in commercial creep furnaces.

Figure 6 – Modified hot MOR test set up for hot compression testing

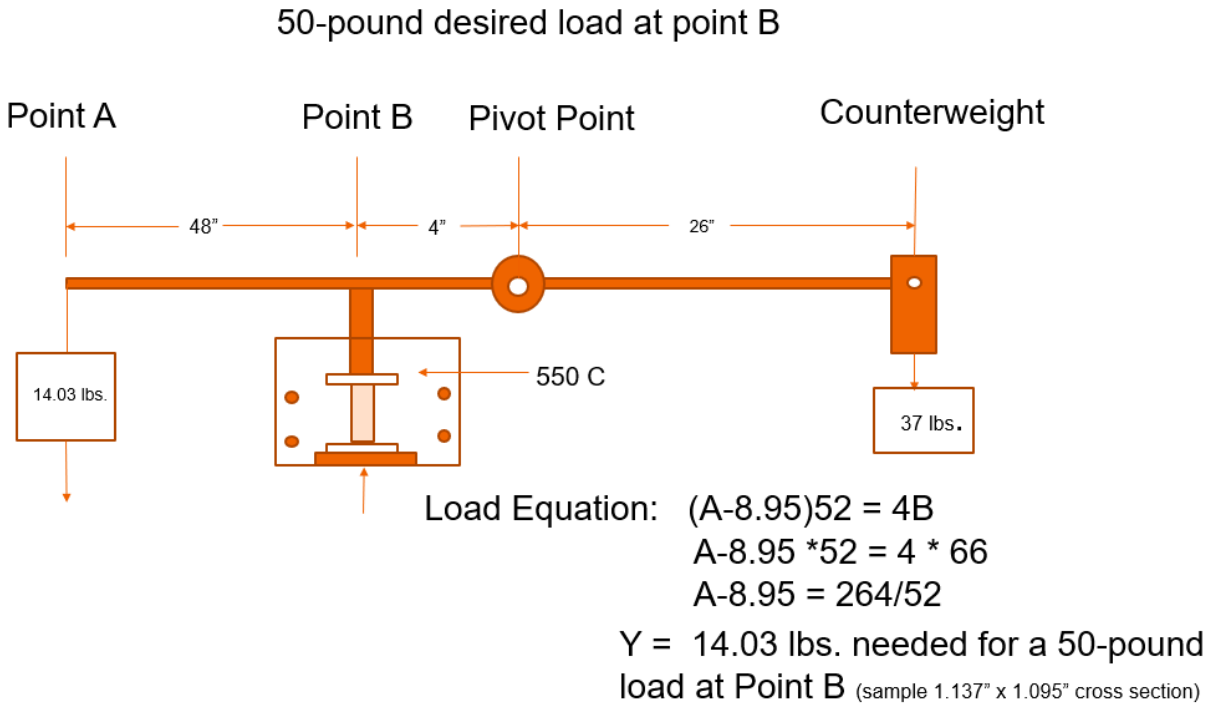


Figure 7 – View of hot compression set up

Ceramic push bar + attachment hardware (7.432#'s) was considered when the beam was balanced.

The weight of the cap plate was also considered in the load calculation.

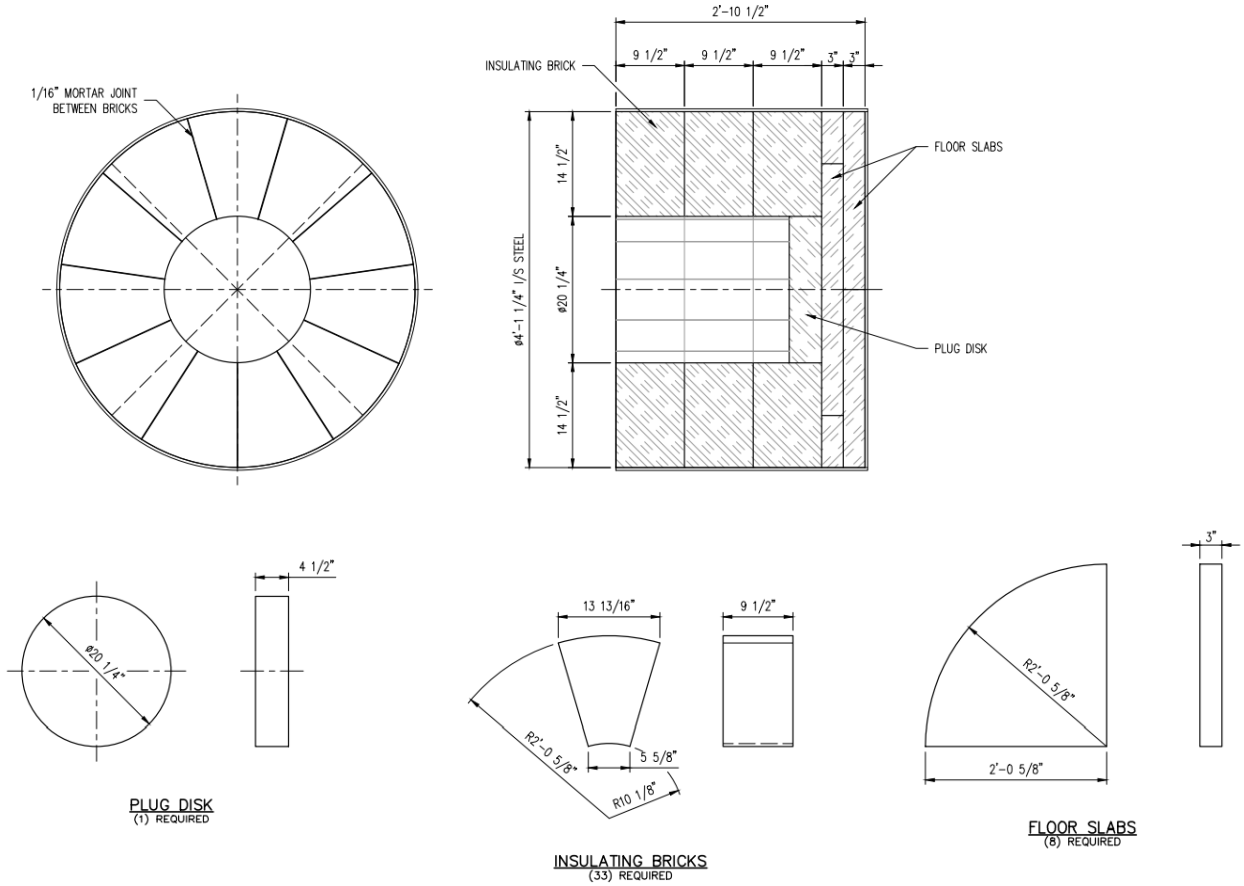
Table 8 – GP-20-3 compressive strengths at given temperatures

Sample	Temperature °C	Time (Hours)	Load (psi)	% Deformation
GP-20-3 w/o salt	550	1-1/2	50	-0.06
GP-20-3 w/salt	550	1-1/2	50	-0.59
GP-20-3 w/salt	550	50	50	-0.34
GP-20-3 w/o salt	720	1-1/2	150	-0.24

Pilot Tank Scale-up

Scaling-up for a pilot molten salt tank evaluation was undertaken. The drawing of the pilot tank lining is shown below along with photos of the key-shaped parts.

Figure 8 – Pilot plant lining and shapes



Cast part in mold Cured part before firing Fired Part (1025°C)

External and internal cracking issues were encountered when doing this scale-up. At the time of this writing (2/13/2013) most of the cracking has been eliminated, but the cracking has not been solved 100%.

Geopolymer Mortar Development and Testing

A Geopolymer mortar is needed to resist molten salt and be compatible with the Geopolymer fired shapes. The mortar consisted of Metakaolin, Sodium Silicate, 10M NaOH and aggregates; Kyanite and Mulcoa 60. The aggregates were necessary to give the mortar the desired consistency for troweling and to provide refractoriness. To test the mortar for bond strength, a 4-point loading strength test was performed as shown below:

Figure 9 – 4-point MOR testing on the geopolymer mortar

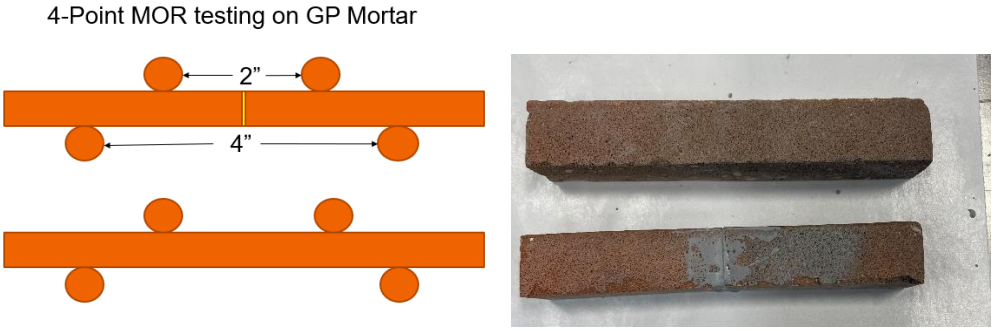


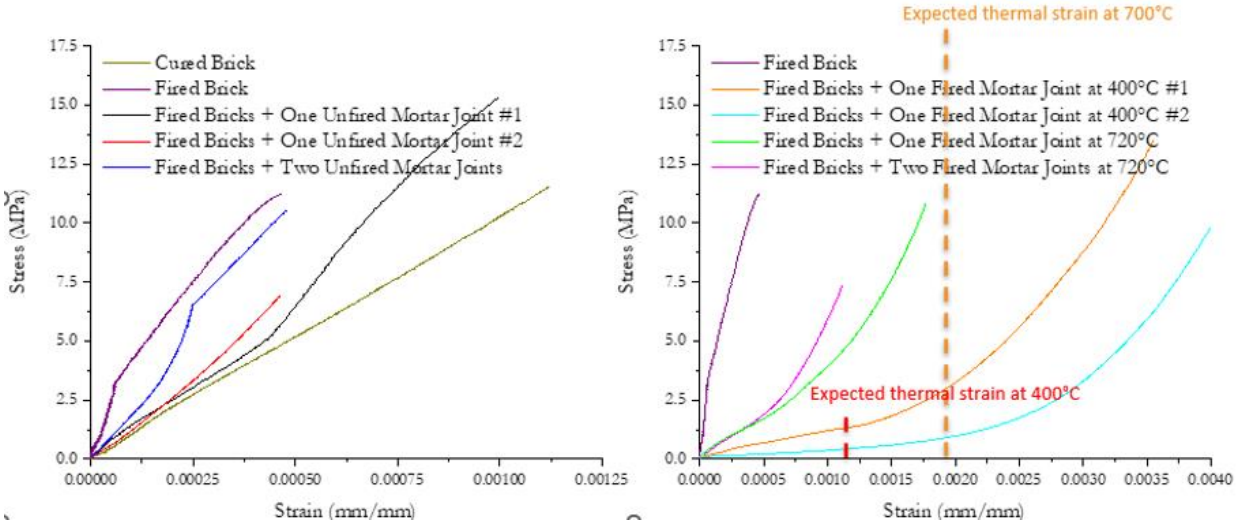
Table 9 – 4 -point MOR data

Sample	MOR (MPa)
Un-Mortared 1050°C Fired Bar (GP-20-3)	1.25
Mortared 1050°C Fired Bar	0.51
Mortared 60°C Cured Bar	1.20

Compression testing was done on mortared cube modules to determine stress/strain information for the lining design.

Figure 10 – Samples for room temperature mortar compression testing

Figure 11 – Mortar joint compression at room temperature



Cured brick vs. fired brick

- Firing makes bricks stiffer (but about the same strength)

Baseline bricks vs. unfired mortar joints

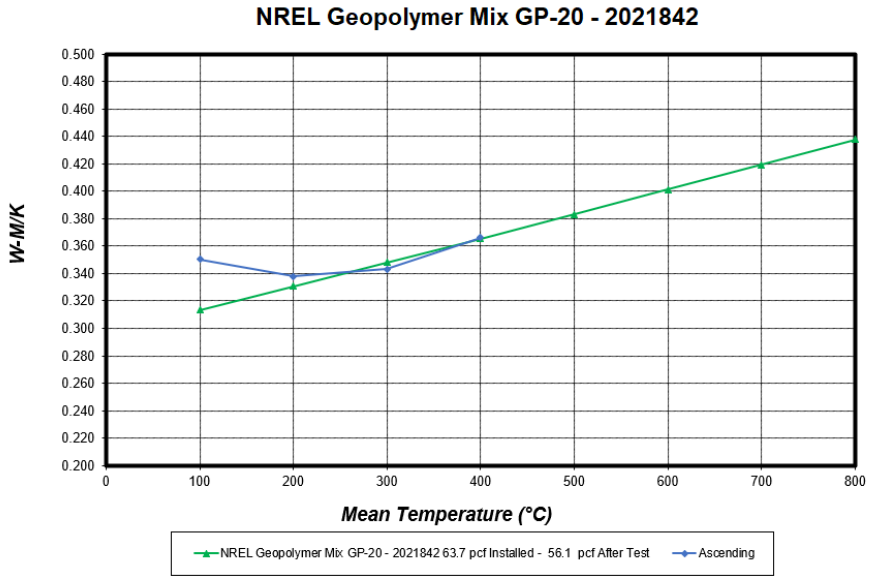
- Generally similar behaviors

Baseline bricks vs. fired mortar joints

- Significantly more deformation from fired mortar layer before cracking
- No obvious strength reduction

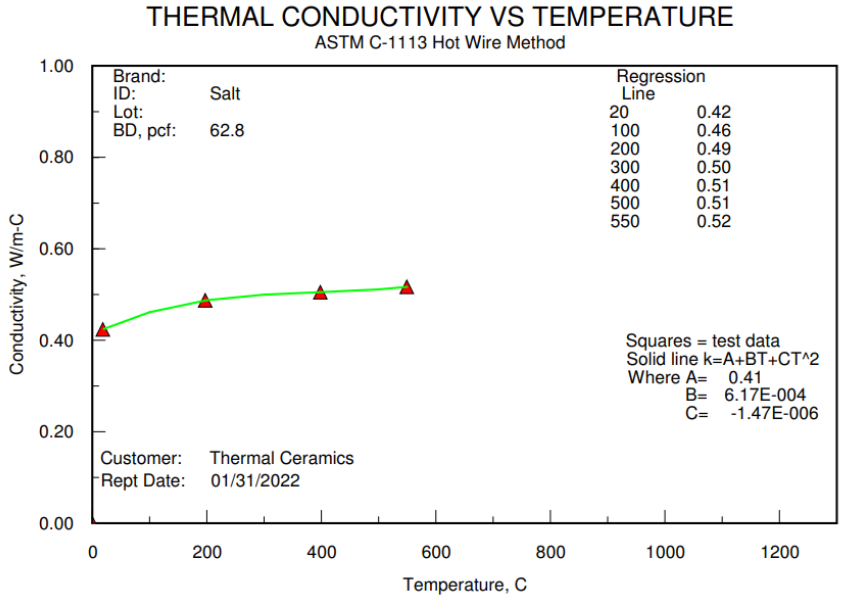
Thermal Conductivity Testing

Figure 12 - ASTM C201 Thermal Conductivity on GP-20 w/o salt saturation



In order to avoid salt contamination in the ASTMC 201 test unit, it was decided to use ASTM C 1113 (Hot Wire) thermal conductivity testing for the GP-20 saturated with salt:

Figure 13 – ASTM C1113 Thermal Conductivity on GP-20 saturated with nitrate salt



Porosity Determination

Initially the porosity was determined by using Isopropyl Alcohol instead of the normal water boiling method. The alcohol method was recommended for Geopolymers by MIT because they determined in past research that there are problems associated with using the water displacement method with products having the Geopolymer bond.

Table 10 – IPA Porosity Values for Cast samples of GP-20-3

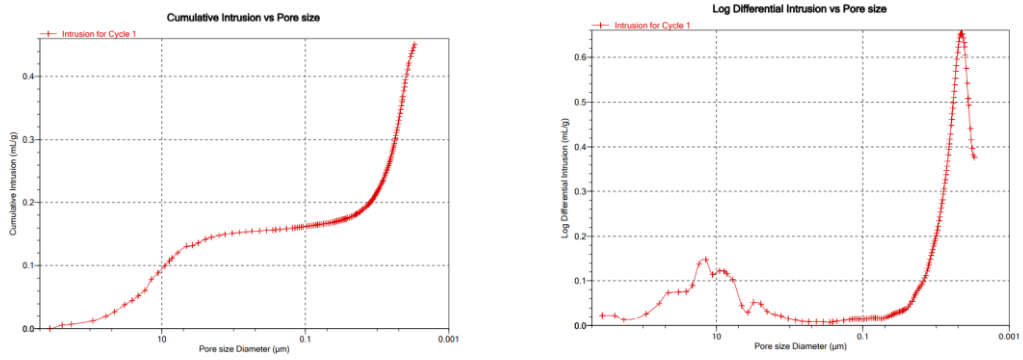
Sample	Heat Treatment	IPA Porosity
GP-20-3	60°C	13.7-20.1
GP-20-3	1000C	5.1
GP-20-3	1100C	7.0

Because of concerns that IPA cannot fully permeate small pores at ambient pressure, it was then decided to determine the porosity with the Mercury Intrusion at Micromeritics Instrument Corporation, located in Norcross, GA. The porosity values were significantly higher than those measured with the IPA method.

Table 11 - Mercury Intrusion Porosity Values for Cast GP-20-3

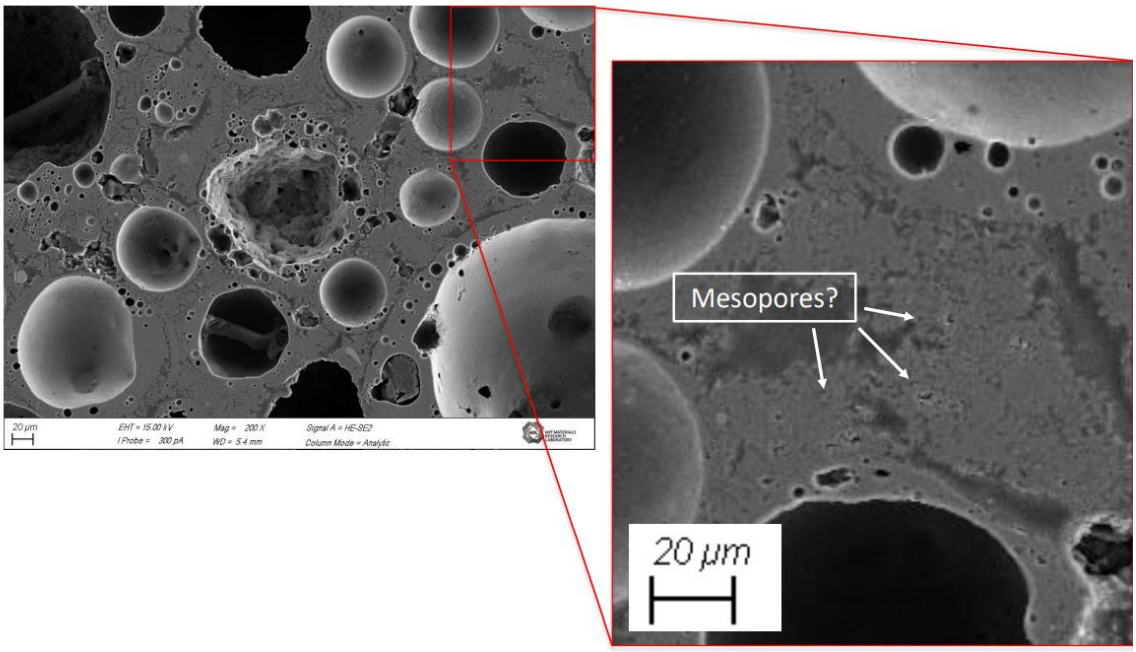
Sample	Heat Treatment (°C)	Mercury Intrusion Porosity (%)
GP-20-3	400	54.9
GP-20-3	950	55.1
GP-20-3	1050	47.0
GP-20-3	1200	59.2

Figure 14 – Porosity size distribution in GP-20-3 by the Mercury Intrusion method



As shown above, the porosity size distribution in the GP-20-3 Geopolymer is bi-modal which agrees with the electron microscopy observation in Figure 14 that shows large micro-pores by the Cenospheres and small meso-pores in the geopolymer matrix. As explained later, this combination of micro-porosity and meso-porosity may contribute to the excellent resistance this product has to molten salt. It should be noted that GP-20-3 samples can float in molten salt which highlights their low bulk density with closed porosities where the salt density is about 1.5 – 1.7 g/cm^3.

Figure 15 – Microstructure of GP-20-3 showing closed porosity and Mesoporosity



Molten Salt Testing

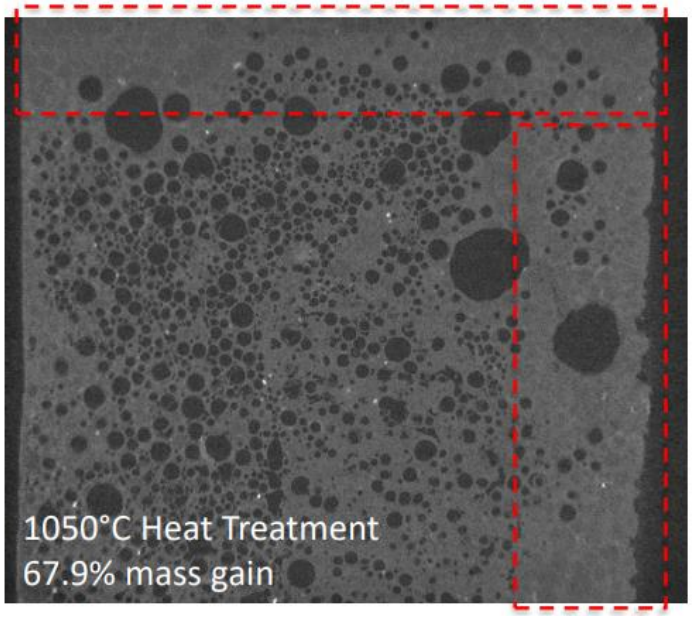
Both nitrate and chloride molten salt immersion testing was performed on samples of GP-20 and/or GP-20-3. Most of the testing was done with the molten nitrate salt because of its lower temperature range for easier handling.

Nitrate Molten Salt

The nitrate salt mixture used in the testing was 60% $NaNO_3$ and 40% KNO_3, known in the industry as “Solar Salt”. The melting range is about 220-230°C and the molten testing was done at 550°C, the projected upper temperature in a thermal energy storage tank with the nitrate salt as the storage media. The thermal conductivity of the solar salt is 0.53 w/m·K at about 550°C, which is not much different than the GP-20-3 when it is saturated with this salt.

As shown by the X-ray computed tomography scan below, it was determined that the nitrate salt permeates the open meso-porosity of the refractory matrix but does not appear to attack the closed porosity formed by Cenospheres during the duration of the testing (15 days (about 2 weeks) of immersion at 550°C). If the thermal conductivity is not significantly compromised by the molten salt permeation, the matrix and frozen molten salt near its melting point in effect becomes the tank liner barrier layer which is similar to molten Aluminum resistant refractory linings where it is critical to have a freeze plane in the refractory lining thickness.

Figure 16 – X-ray computed tomography scan of GP-20-3 saturated with molten Nitrate Salt for 30 days at 550°C



Conclusions

It can be concluded from this research that a medium-density Geopolymer refractory was developed that resists chemical attack from molten nitrate and chloride salts. The refractory does not resist saturation, but like a ceramic sponge it holds the molten salt and then with correct lining design the molten salt will freeze within the refractory where the molten salt impregnated refractory becomes an effective barrier. The refractory developed in this study has the advantage of low thermal conductivity even when saturated with the salt. It also has excellent strengths at the operating temperatures of molten salt thermal storage tanks when unsaturated or saturated with the salts. Testing in a pilot tank is recommended.

References

[1] SQM, “SQM’s Thermo-Solar Salts: The Natural Solution for Thermal Storage and Heat Transfer in Your CSP Plant.” .

[2] Y. Zhao, “Molten Chloride Thermophysical Properties, Chemical Optimization, and Purification Purification,” 2020.