

# MICROWAVE ENHANCED DRYING AND FIRING OF GEOPOLYMERS

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## ABSTRACT

The feasibility of using microwave energy to dry and fire pre-cured geopolymers was experimentally demonstrated, and supported by analysis of published microwave dielectric data for geopolymers. Dielectric loss tangents and half power microwave absorption depths were calculated from published room temperature dielectric constant and loss values of various geopolymer compositions. The published data indicated that geopolymers would heat at room temperature with microwave energy. Several laboratory experiments were performed to test the heating behavior of sodium and potassium based geopolymer compositions. Experiments demonstrated more vigorous microwave heating with sodium geopolymers than with potassium geopolymers. Both compositions were dried in less than 10 minutes with pure microwave heating. Further heating with pure microwave energy resulted in non-uniform, rapid heating, or “thermal runaway”, with localized melting of the geopolymer. Hybrid microwave heating with susceptors resulted in uniformly fired geopolymers, without melting.

## INTRODUCTION

Interest in geopolymers has accelerated in recent years due to their possible use in structural applications, dentistry, and hazardous waste stabilization, while maintaining a trivial environmental impact compared to traditional building materials. Many useful geopolymer compositions are fabricated by low temperature chemical reaction based curing processes<sup>1-3</sup>. Some recent research has been reported for using microwave energy to enhance curing and drying<sup>4, 5</sup>. Other research has focused on high temperature firing of geopolymers, which can develop stronger glass-ceramic materials<sup>6-8</sup>. In situations where heat is required, as in drying and firing, microwave energy provides an energy efficient alternative in place of conventional heating. Traditional radiant heating methods rely on thermal conduction to deliver heat throughout a material. Microwaves generate heat throughout the volume of the material, allowing faster, more uniform heating to occur. Volumetric microwave heating helps to overcome sluggish endothermic phase transitions, such as evaporation of water or decomposition of kaolin to metakaolin through the loss of hydroxides. Both drying and dehydration occur in the firing of geopolymers. In traditional heating, these reactions often require slow heating, as the endothermic reaction prevents heat from progressing into the product until the reaction completes first at the surface. Microwaves can generate heat throughout the part despite an endotherm<sup>9</sup>.

When microwave energy is the sole source of heat, a material that absorbs microwave energy will heat volumetrically, but cool from the surface. This situation creates an “inverse temperature profile” in which the sample is warmer inside and cooler at the surface during heating. This is opposite of traditional radiant heating where the material will be cooler in the center. In some materials, the inverse temperature profile can lead to thermal runaway – where the hotter center heats better than the cooler surface, and in turn heats better in the microwave. The thermal runaway can lead to molten centers with unfired surfaces.

The most practical way to prevent thermal runaway is through hybrid microwave heating. Hybrid heating combines a radiant heat source with microwave energy, providing a uniform temperature profile throughout the sample as heat is generated at the interior while heat conducts from the exterior. This combination results in a uniform temperature profile and in turn improved properties. Two types of hybrid heating are susceptors, and Microwave Assist Technology (MAT). Susceptors function like wireless microwave heating elements, efficiently converting microwave energy into heat. When used with insulation thermal packages, susceptors can be used to fire ceramics even in standard kitchen microwaves<sup>10</sup>. MAT is based on traditional kilns and uses gas or electric radiant heat, which is controlled independently of the microwave energy<sup>11</sup>. MAT generally requires less microwave power, which reduces equipment costs and simplifies scale-up<sup>12</sup>.

### Dielectric Properties

The effectiveness of microwave heating for materials is generally determined by the dielectric properties at the microwave frequency. Two values represent the dielectric properties of a material, dielectric constant,  $\epsilon'$ , and dielectric loss,  $\epsilon''$ . Dielectric constant represents the ability for ions and dipoles within a material to polarize in response to an alternating electric field, and also determines the wavelength of the microwave energy within the material. The dielectric loss represents the degree to which an alternating field is converted to heat energy. From these two values can be derived the loss tangent,  $\tan \delta$ , and the half-power depth. A loss tangent between 0.01 and 1 generally indicates that a material will heat well with microwave energy. Below 0.01, materials tend to be microwave transparent, while above 1 materials become reflective<sup>13</sup>. The half power depth measures the distance at which 50% of the microwave energy passing through a material is dissipated. The equations for loss tangent (1) and half power depth (2) are expressed below. In equation 2,  $D_{HP}$  is the half power depth,  $c$  is the speed of light,  $\omega$  is the angular frequency ( $2\pi f$ ), and  $\epsilon_0$  is the permittivity of free space.

$$\tan(\delta) = \frac{\epsilon''}{\epsilon'} \quad (1)$$

$$D_{HP} = \frac{c(\ln 2)}{2\omega\epsilon_0} \left( \frac{2}{\left( \sqrt{1 + (\tan \delta)^2} - 1 \right) \epsilon'} \right)^{1/2} \quad (2)$$

Published room temperature dielectric data was obtained from Jumrat et al<sup>5</sup>. From this data, loss tangent and half-power depth could be calculated to determine support for microwave heating from room temperature. Geopolymers are composed significantly of both free water and hydroxides surrounding charge balancing alkali cations. These structures suggest strong likelihood for geopolymers to heat well with microwave energy, with mobile water dipoles and ions. The Jumrat paper presented just  $\epsilon'$  and  $\epsilon''$ , and data was measured as a function of curing time. As the geopolymer cured, the dielectric loss and dielectric constant both decreased, suggesting reduced mobility of polar groups as curing progressed. Ceralink selected two of the data sets to calculate the loss tangent and half power depths. These calculations strongly supported microwave heating of geopolymers from room temperature (Figure 1).

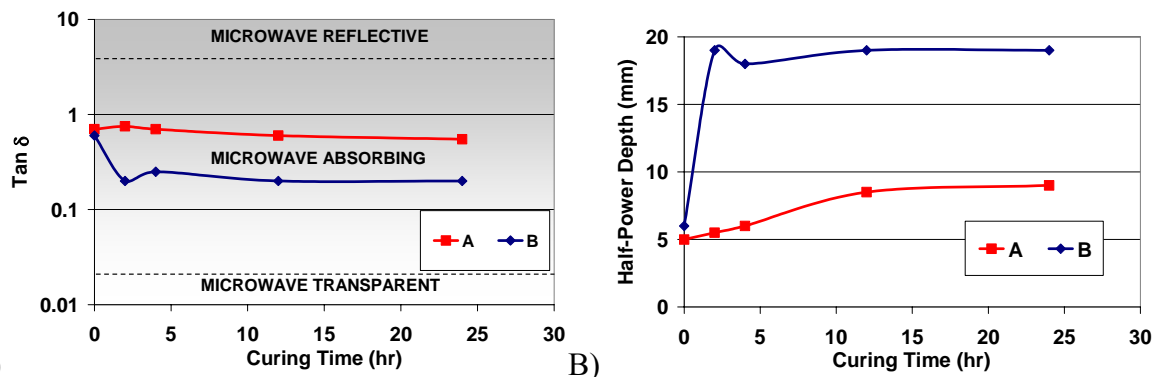


Figure 1: A) Loss tangents calculated for two representative sodium-based geopolymer compositions reported by Jumrat, et al. B) Half-power depth for the two geopolymer compositions.

The loss tangent values determined by the present authors from Jumrat’s data were between 0.1 and 1.0, indicating that these geopolymer materials will heat very well in microwave, at least from room temperature. The half-power depth indicates that the microwave energy transmits farther into the material as curing completes. This heating is likely due to the presence of water molecules within the crystal lattice and the charge balancing cations, in this case sodium. At elevated temperatures after drying, the cation is likely the greatest contributor to suspending action, as water and hydroxides are thermally removed from the geopolymer structure by approximately 400 °C, as shown by Bell, et al<sup>7</sup>. In order to understand microwave heating above room temperature, high temperature dielectric measurements will be required. These will be investigated in future studies.

This study investigated experimental microwave heating of geopolymers with sodium and potassium charge balancing cations. The effect of the alkali cation used in the geopolymer was studied through the laboratory experiments. Microwave firing of a potassium based geopolymer with basalt fiber reinforcement was also studied. Microwave heating was explored with microwave as the only source of heat to the geopolymer, and also with a hybrid susceptor-based method.

## EXPERIMENTAL PROCEDURE

Pre-cured sodium and potassium-based geopolymer samples were weighed and dimensions measured before being placed in an alumina fiber thermal package for heating experiments. Some of the potassium-based geopolymer samples were reinforced with 7 wt % chopped basalt fibers. The thermal package was made of 2.5 cm thick Unifrax Duraboard 2600<sup>®</sup> insulation cylinder, with 4 cm thick base and lid, and 8 cm inner diameter. The geopolymer sample was placed on a bed of alumina powder in an alumina crucible in the center of the thermal package. The thermal package allowed room for adding two 25 gram silicon carbide (SiC) susceptors (Research Microwave Systems “Thermcepts”) for hybrid susceptor-assisted heating studies. Figure 2 (A and B) shows schematics of these set-ups without and with susceptors, respectively, compared to photographs of the set-ups as used for experimentation (Figure 2 C and D). The geopolymer composites here examined were prepared and studied by Rill et al. and the findings were published elsewhere.<sup>14</sup>

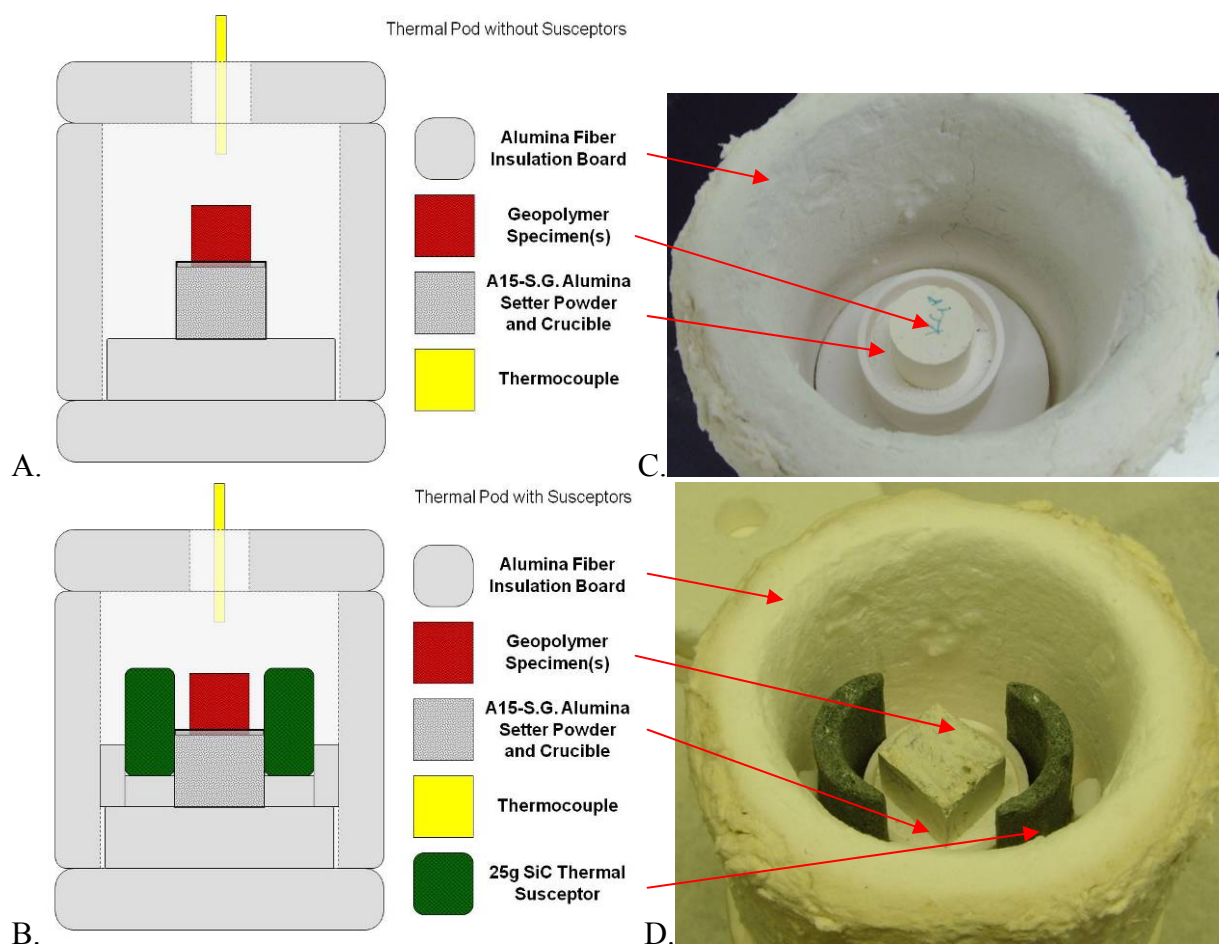


Figure 2. Schematics of A) Alumina fiber thermal package without suscepting material, used for “pure” microwave heating. B) Alumina fiber hybrid thermal package with two 25 g SiC susceptors positioned on either side of sample and setter. C) Photograph of thermal package without SiC susceptors. D) Photograph of thermal package with susceptors. Both set-ups used A15-S.G. alumina powder contained within an alumina crucible as a setter. A thermocouple was extended through the lid, and positioned approximately 1.5 cm above the sample.

Four experiments (Table I, 1-4) were performed to study the feasibility of drying sodium and potassium based geopolymers via direct heating, i.e. without the use of suscepting material (Figure 2A and C). Samples were arranged within a Research Microwave Systems ThermWave 1.3 microwave system (2.45 GHz, 900 W maximum power) chamber and microwave energy was applied for 15 minutes, ranging from 20% power (180 W) to 50% (450 W), with the same power-time profile for each sample. Temperature within the chamber was recorded via the thermocouple. Once the samples were cooled, final weight and dimensions were measured.

Four experiments were used to study the firing of potassium-based geopolymer with basalt fiber reinforcement. Direct microwave heating was used in one experiment, while experiments 6-8 employed SiC susceptors within the thermal package (Figure 2B). Target firing temperatures for samples 6, 7, and 8 were 800, 900, and 1000 °C, respectively and were weighed, measured, and cross-sectioned vertically to observe the interior structure once cooled. The temperature within the chamber was recorded via the thermocouple. An optical pyrometer with an emissivity setting of 0.90 was used after heating to determine the actual sample temperature after the microwave power was stopped. Sample descriptions are provided below in Table I.

Table I: Descriptions of geopolymer (GP) microwave heating experiments for drying and firing sodium and potassium based geopolymers.

Experiment No.	Experiment Purpose	Geopolymer Sample Composition	Geopolymer Mass (g)	Heat Treatment Temperature (°C)
1	Drying, self-heating	Na-based geopolymer	2	114
2	Drying, self-heating	Na-based geopolymer	16	209
3	Drying, self-heating	K-based geopolymer	16	143
4	Drying, self-heating	K-based geopolymer, Basalt fiber reinforced	16	123
5	Firing, self-heating	K-based geopolymer, Basalt fiber reinforced	16	560
6	Firing with susceptors	K-based geopolymer Basalt fiber reinforced	16	800
7	Firing with susceptors	K-based geopolymer Basalt fiber reinforced	16	900
8	Firing with susceptors	K-based geopolymer Basalt fiber reinforced	16	973

## RESULTS AND DISCUSSION

### Geopolymer Microwave Drying Experiments

Heating curves for drying experiments are provided in Figure 3. The drying experiments revealed the difference in heating ability for sodium and potassium based geopolymers. The sodium composition heated much faster than the potassium based sample of equal mass, reaching over 70 °C higher temperature in the 15 minute experiment. This may be due to a higher mobility of the smaller sodium ion than the potassium ion. Dielectric property measurements of these two compositions would be extremely interesting to determine how these cations affect the properties of the geopolymers.

Another effect observed in the drying experiments was a mass effect, in which 16 grams of sodium geopolymer, heated the thermal package much more than a 2 gram sample. This mass effect is unsurprising, as the geopolymer was the only source for heating in the thermal package volume.

The basalt fiber reinforced, potassium based geopolymer heated more slowly than the unreinforced sample. Basalts have a wide range of chemical compositions, and therefore a range of microwave heating ability. In this case, the basalt appeared to heat less than the geopolymer, resulting in the slower microwave heating.

The sodium geopolymers had an average mass loss of 12%, while the unreinforced potassium geopolymers lost 13%. The reinforced potassium geopolymer, meanwhile, lost only 5.4% mass, despite reaching higher temperatures than the unreinforced sodium sample. Minor cracking was observed in some of the dried samples, however all samples remained intact.

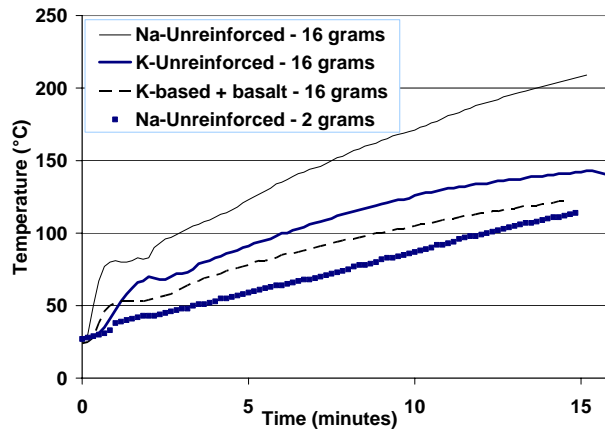


Figure 3: Heating curves for samples 1-4. All samples were ramped uniformly from 20% to 50% power. These temperatures were measured by the thermocouple positioned 1.5 cm above the geopolymer sample.

### Geopolymer Microwave Firing Experiments

The microwave heating profiles from the firing experiments of K-based geopolymers with 7 wt% basalt fiber reinforcement are provided in Figure 4. One sample was heated with microwave-only heating. This sample reached 200 °C in approximately 20 minutes, after which the heating rate accelerated quickly for 1-2 minutes prior to an arc. The electrical discharge (arc) provided a basis for terminating the experiment. The remaining samples were heated with susceptors to 800, 900, and 1000 °C, without any incidence of arcing.

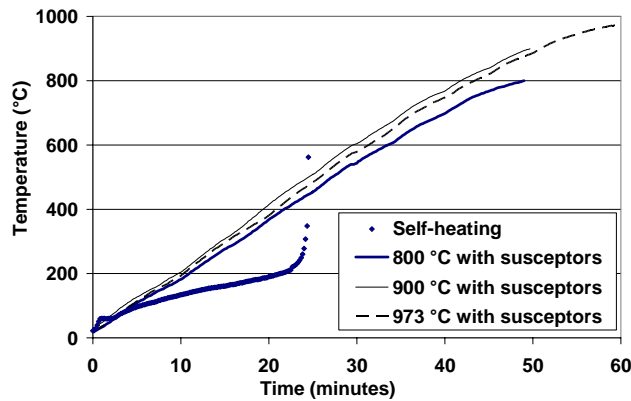


Figure 4: Heating profiles for the microwave firing experiments. All samples were K-based with 7% basalt-fiber reinforcement.

The self heated sample only registered temperature at the thermocouple of up to approximately 550 °C immediately prior to arcing. However, upon examination of the sample (Figure 5), it was found that significant thermal runaway had occurred. The interior of the sample had melted, resulting in glassy bubbles and flow of the molten geopolymer, down into the alumina setter-powder. The molten region indicated that temperatures in excess of 1160 °C (the highest temperature achieved on susceptor fired materials, at which no melting was observed) had been achieved within the sample. Despite this intense internal heating, the top and side surfaces of the sample appeared as though they had not been fired. A cross-section of this sample revealed a dramatic example of an inverse temperature profile, leading to thermal runaway. This experiment lead to speculation that the dielectric loss and loss tangent of this geopolymer increases substantially as temperature increases. A shift to higher dielectric loss with increasing temperature would direct more microwave energy into the hotter

material. The hotter regions, then would heat faster, meanwhile the less absorbing, cooler sample surfaces lose heat to the cold environment in the thermal package. This situation of “thermal runaway” has been observed and reported by several authors with microwave heating of many other materials systems<sup>15-17</sup>. The literature on thermal runaway supports the assumption of increasing dielectric loss, as well as the use of hybrid heating (e.g. susceptors) to prevent runaway. High temperature measurements of the dielectric properties of these materials are planned as future work to confirm this assumption. While melting and a non-uniform cross section were not desired, this experiment strongly demonstrated the feasibility of rapidly heating geopolymers to firing and melting temperatures using microwave heating.

It is also worthwhile to point out that geopolymers are nanoporous having 41 vol % porosity, with an average pore size of 3.4 nm radius and the porosity is closed rather than interconnected<sup>18, 19</sup>.

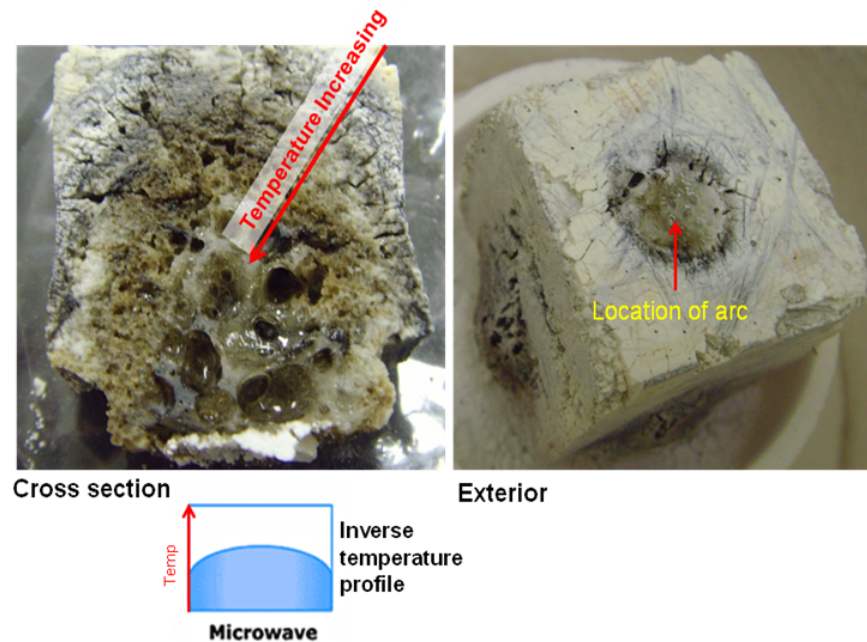


Figure 5: Photograph of microwave self-heated potassium geopolymer with 7 wt% basalt fiber reinforcement, after cross sectioning. The cross section shows dramatic evidence of the thermal runaway, in which the center of the sample melted and flowed down into the alumina powder bed. The exterior view of the sample shows essentially unfired geopolymer over most of the surface, with bulges at the centers of the sample faces resulting from the bubbles in the molten geopolymer. A schematic of the inverse temperature profile is shown below the cross section photograph.

The remaining samples 6-8 were fired with susceptors, in order to prevent thermal runaway. Hybrid firing with susceptors resulted in significantly more uniform cross sections than were seen with pure-microwave heating. Furthermore, the susceptor heated samples did not appear to contain any molten regions. Sample 8 was fired to the highest temperature, reaching 973 °C at the thermocouple. The sample temperature was measured to be 1160 °C by the optical pyrometer, immediately after the end of the microwave power application. This sample appeared to have the least cracking, the greatest shrinkage, and was noted to be more resistant to cutting than the samples fired at lower temperatures. The cross section and exterior of the susceptor fired geopolymer sample are shown below in Figure 6.

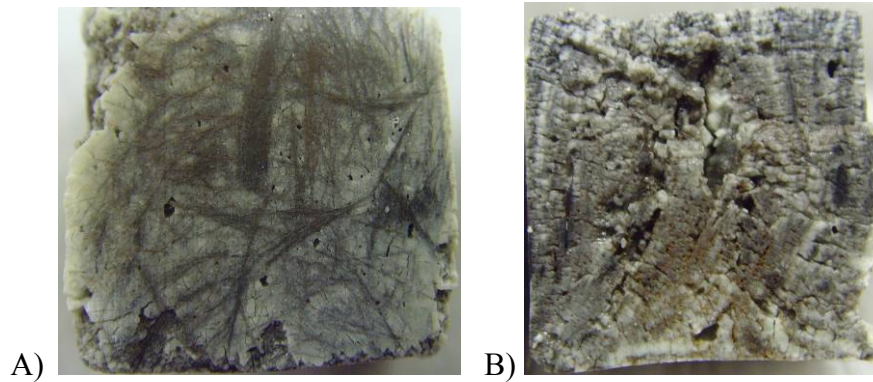


Figure 6: Photograph of A) exterior and B) cross section of Sample 8 after hybrid microwave-susceptor firing to a surface temperature of 1160 °C.

## CONCLUSION

Loss tangent and half-power depth were shown from the dielectric constant and loss of fly-ash based geopolymers. These dielectrics support the use of microwave energy for heating geopolymers to significant temperatures, as successfully demonstrated by laboratory experiments. Four geopolymer compositions were heated with pure microwave energy and achieved temperatures over 100 °C in less than 10 minutes time. In comparing geopolymers with similar mass but varying cation, an ion effect was observed where the smaller sodium ion resulted in faster heating than did potassium. Pure microwave energy was utilized to rapidly heat a K-based, basalt-reinforced geopolymer to significantly above its glass-ceramic transition temperature, with an inverse temperature profile. The dielectric properties of the K-based geopolymer were predicted to increase rapidly and dramatically above ~500 °C. Three additional samples of the same composition were fired to thermocouple temperatures of 800, 900, and 973 °C with the inclusion of susceptors to provide a radiant heat source. Hybrid heating was shown to produce uniform temperatures throughout the samples, preventing thermal runaway and resulting in uniformly appearing samples.

## ACKNOWLEDGMENTS

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