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Printed Carbon Nanotube and Graphene Heaters for drying ceramics

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The ceramic manufacturing process has been subject to many advances with the evolution of new technologies. However, there are still some delays and losses in the fundamental process which may be mitigated by deploying alternative technical tools and methods . One such stage is the sensitive pre-drying phase in which ceramic bodies can sustain drying defects such as micro-cracking and fractures due to lack of fine process control. This project investigates the feasibility of using Longwave infrared (LWIR) radiation emitted by a printed Carbon Nanotubes and Graphene (CNTG) heater for pre-drying a clay sample. The CNTG heater emits infrared radiation with a relatively low DC voltage power supply. By radiant heat transfer, homogeneous and uniform drying has been observed in the sample. The penetrative capability of the infrared energy which warms the inside of the sample is presented, as along with the results of comparing the CNTG heater with a Silicon mat heater that also emits infrared radiation. The study establishes that the CNTG heater is not only capable of reducing the lead time of ceramics drying using penetrative IR, but also as an efficient and versatile option that can be economically deployed in the pre-drying stage of a ceramic manufacturing process.

Keywords: Graphene and Carbon Nanotubes, Infrared Radiation, Ceramics, Drying

1. Introduction

Ceramic manufacturing is one of the oldest industries known to mankind. In modern times, the production method has been long-established, and the processes involved have adopted technologies and practices that aim to increase productivity whilst minimising waste. Control and monitoring of several processing conditions are taking place in manufacturing plants to ensure the minimisation of process and product waste. This includes the careful handling of the freshly demoulded ceramic products of various shapes, known as green bodies, which inherently carry a high amount of moisture and thus are prone to plastic deformation under even minor pressure [1]. In principle, the moisture content must evaporate steadily and uniformly in order to minimise any differential stresses in the green body that can cause hairline fractures and lead to product defects [2]. However, microclimatic conditions in production plants, such as ambient temperature, airflow and relative humidity can be highly irregular and combined with the natural variation of the ceramic materials, frequently result in subpar conditions for uniform moisture evaporation during the drying stage [3]. Traditionally, product defects in ceramics plants tend to be high (in comparison with other manufacturing industries) with waste (total loss) accounting for more than 15% of the total yearly production [4].

There is reason to believe that the deployment of low-energy Long-Wave Infrared Radiant (LWIR) to supply highly directional heat to freshly casted ceramic green bodies could be a viable method of effectively and uniformly pre-dry ceramics before entering the main convection-drying part of the manufacturing process. Despite their potential, the utilisation of IR heaters has proven to be largely impractical in many manufacturing plants [5], due to the size and geometrical constraints of the conventional materials such heaters are traditionally fabricated from, comprising of bulky and expensive metal structures. Recent advances made in carbon nanotubes and graphene (CNTG) printable inks [6], could enable the development of flexible LWIR heaters due to the novel electric properties of these carbon particles. Such speciality inks can be printed on several different easy-to-fabricate substrates and using low voltage electricity [7] could offer new IR pre-drying possibilities for ceramics that have until now been costly and/or technically complex.

This research aims to develop and test the feasibility of a heater utilising carbon nanotubes and graphene to supply directional and penetrative Longwave Infrared (LWIR) heat. This should provide energy to pre-dry ceramics by allowing the removal of moisture in a uniform fashion, necessary to achieve 5% of drying shrinkage. This could specifically benefit high value and high volume ceramic manufacturing were the economics of controlled pre-drying is of substantial interest as this process does not require large capital investment or energy, unlike large industrial microwave ovens.

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2. Background

The mechanism of drying a wet ceramic body involves water evaporation. The drying rate can be explained as the rate of moisture loss through evaporation per unit of time. In the manufacturing process, drying is usually carried out in two stages. Pre-drying and main drying. Pre-drying is an important phase in ceramic production during which clay plasticity is eliminated and achieves 80-100% of drying shrinkage. Ford [8] states that the drying behaviour of ceramics consists of different phases characterised by milestone points concerning moisture content. At the critical moisture content (CMC) point, further shrinkage of the green ceramic body stops and its drying rate begins to decline. Drying shrinkage occurs when the reduction of water which takes place over an extended period of time results in a reduction in weight. Pre-drying reduces the sudden shrinkage that can lead to the formation of cracks and fractures in the green body from the high temperature of the main dryers. Slow and gradual evaporation of moisture content during pre-drying avoids losses in drying. Shrinkage while drying is significantly one of the most critical factors for the quality control of ceramic products. The contemporary approach to pre-drying observed in a very large ceramic plants involve keeping the cast green bodies for several hours in a holding area (mainly on very slow-moving conveyors) on the shop floor before routing them to an air convection drying tunnel. This can lead to high irregularity due to the factory's variable ambient environment. Moreover, water evaporation can occur more from the surface of the drying item rather than uniformly from the whole body. This can cause differential shrinking between the exterior and interior wall surface of the ceramic body, generating cross-body tension resulting in micro-fractures that can be detrimental to the quality and as it can lead to total loss after final production [9].

In order to evaporate the water from the ceramic green body at a faster and more uniform rate, heat energy input is required. For instance, the enthalpy of vaporization of water at standard atmospheric pressure is 2260 kJ/kg [10]. Supplying heat to evaporate the water could be achieved by any of the three modes of heat transfer: convection, conduction, and radiation or by a combination of them [8]. The present study focuses particularly on radiative drying of ceramics and offers a more detailed review of the radiant heating characteristics and effects. Penetrative infrared radiation directed to the green body can warm the interior of the solid and it is generally advantageous as a uniform and efficient heat transfer method. Radiant heat is the emission of electromagnetic waves from any matter that has a temperature greater than absolute zero. Radiant heating technology is defined as the method of intentionally using the principles of electromagnetic radiation to transfer energy from an emitting heat source to another object. Its application can be seen in numerous industries including food, paper and powder processing [11]. Ford [8] claims that a ceramic that is dried under infrared radiation behaves the same as when dried with convection.

Infrared radiation (IR) is a type of electromagnetic radiation with wavelengths between 700 nanometres and 1 millimetre, making it lie between visible light (shorter wavelengths) and microwaves (longer wavelengths) in the electromagnetic spectrum. IR waves are highly directional and travel in straight lines which means that the direction of incident waves upon heating a surface may alter how the radiation reacts with it. Radiation falling on a particular object will get absorbed, reflected, and transmitted. The division of radiation into these three outcomes will mainly depend on the emissivity (ε) of the material. The absorbed radiation is converted to heat energy which will transmit further through the object via conduction and convection [12, 13]. In the instance of using IR to supply heat, radiation is initially absorbed in the surface layer of the object. Subsequently, radiation penetrates to some depth in moist, porous materials. The ability of IR waves to penetrate bodies depends on several factors, including primarily moisture content [14]. This is because water is a great absorber of infrared on account of the presence of O-H bonds, which begin to vibrate at specific frequencies of radiation within the IR part of the electromagnetic spectrum.

The process of converting IR into dipole bond molecule oscillations causes water to evaporate as the kinetic energy imparted in the O-H bonds enables phase change from liquid to vapour [15]. According to Qassem and Kyriacou [16], as the wavelength increases and the spectrum moves deeper into the infrared region, the behaviour of liquid water tends to change remarkably and becomes exceptionally absorbing of radiation. Consequently, the decision to experiment with utilising LWIR is seemingly fitting. According to Woods and Wiedemann [17], the water molecule is Infrared active, meaning that it will bend or stretch causing them to overcome the Van Der Waals forces attracting them together thus enabling water to change phase.

Carbon nanotubes and graphene (CNTG) are known for many novel properties. The main reason for choosing graphene as a radiation element is due to its high emissivity, thermal conductivity and resistivity. Current literature on heaters made out of CNTG is sparse. Grzegorz Wroblewski et al. [18] used spray-coated multi-walled carbon nanotubes and graphene (MWCNTG) as a transparent heater for a glass panel. The successful spraying, proved that nanomaterial coating is a promising and cost-effective approach for fabricating large-area heated glass. In addition he confirmed that CNTG coatings can be thermally stable and used for varied applications due to their physical and chemical properties including electrical conductivity and radiant heat emissivity. Moreover, according to research conducted by Patsavellas et al. [7], an engineered CNT and Graphene (CNTG) ink mixture was sprayed and cured on the surface of a thin cementitious board (in an area of 50 cm^2) and proved to be an effective electrical LWIR heater emitting radiant heat, reaching 40 ºC in 2 minutes at very low DC voltage (8V). However, apart from industry specific press ,a thorough literature survey revealed a research gap on the topic of CNTG deployment as radiation elements for controlled pre-drying of ceramics.. Therefore, a rigorous experimentation method was conducted to ascertain the viability of using CNTG for such purpose. This is presented in the next section.

3. Methodology

Establishing an effective study of the practical potential of an IR CNTG heater in the specific application, required a methodical approach to conducting relevant and rigorous experiments in order to meet the stipulated objectives. Roy and Sutapa [19] state that to study a large number of variables (factors) that impact a given process, a cause-effect relationship should be established that describes how each factor causes a change in response. Using Design of Experiments (DOE) can reveal the possible relationships by establishing function(x) variables = y response. This allows for the factors that cause notable changes in the response (outcomes) of a specific process to be clearly understood by sequential experimentation following a statistical analysis of the results.

Oummadi, Siham. [1] states that the uncontrolled evaporation rate in clay can lead to defects like cracking and voids in the ceramic body. The objective of conducting the experiments is

- To control the drying rate during the pre-drying stage of the cast ceramic green body.
- To avoid micro cracking and voids in the ceramic.
- To minimize the lead time of the pre-drying process.

Patsavellas et al. [7] established that small DC voltages applied to a printed CNTG film material will cause it to emit LWIR heat energy that can penetrate a solid body. Deploying this principle in a suitably designed heater could achieve the desired moisture evaporation at an accelerated but controlled rate while homogeneously pre-drying the green body.

Therefore, the experiments were designed as follows:

1. Sequential experimentation was the chosen method. By conducting a series of experiments, observational data could be collected to establish f(X) = Y.
2. The measurable primary response variables were the loss on drying of the green body and the temperature produced by the heater.
3. The drying rates results were analysed using a regression model which is a powerful statistical tool that establishes the correlation between the control variables and response variables by predicting the appropriate input for the desired output.

The project progressed from focusing on the sole use of a CNTG heater to a comparative approach involving a commercially available silicon heater mat which could act as a radiant heat source and was tested in the same manner as the CNTG heater. Both heaters are shown in figure 1. It is worth mentioning that the CNTG heater had its underside painted entirely using a proprietary screen-printing method which deposited a very thin layer along the whole the surface of a Perspex structure using a liquid carrier. Therefore, to achieve a like for like comparison between the two heaters only the top section of the CTNG heater was supplied with voltage and not its sides.

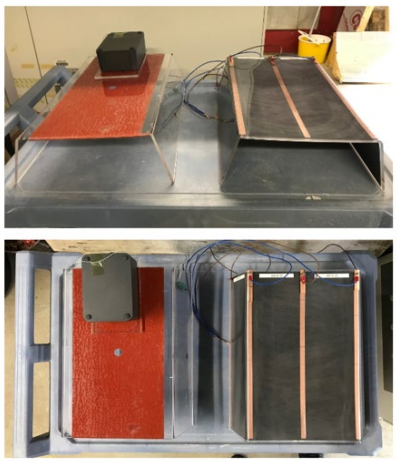

Figure 1 Silicon heater (Left) and CNTG heater (Right)

The experimental set up was established specifically for testing a variety of radiant heat sources with the purpose of pre-drying ceramic green bodies (Lids) as shown in figure 2. According to the capability of conducting this experiment, the heater has been designed as a trapezium-shaped “hood” open at the two long sides in order to allow humidity to escape freely. This hood, fabricated out of clear Perspex material was sprayed with the specially formulated CNTG ink. The green body ceramic cistern lids were placed on a drying rack as shown in figure 3 to reduce surface contact that could block water vapour from escaping from underneath the lid. A digital scale was placed under the lid and the heater to measure the weight loss which was recorded for analysis. Moreover, sensors connected to dataloggers were used to collect temperature and humidity readings. An infrared camera was utilized to capture thermal imaging of the heating process as it occurred to enable the researchers to observe and monitor the homogeneity of the heating as well as the presence of any cold spots.

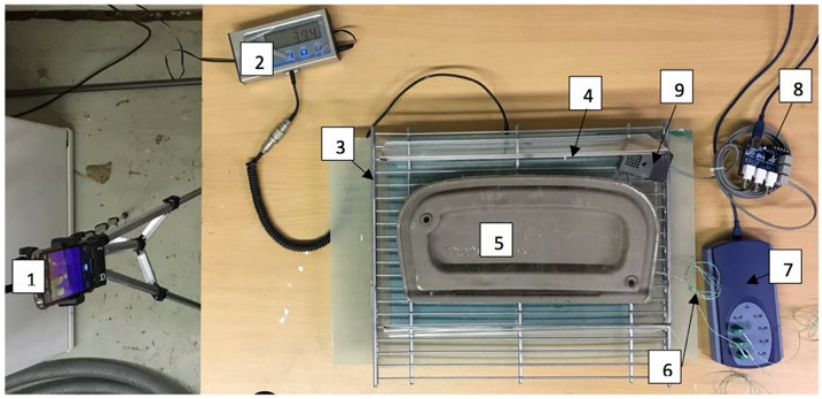

Figure 2 experimental set-up. (1-infrared camera on a tripod, 2- digital scale, 3-drying rack, 4-heater hood, 5-Lid (green body), 6- K type thermocouples, 7- temperature data logger (TC-08), 8- Humidity Datalogger (Dr Daq), 9- Dr Daq humidity sensor)

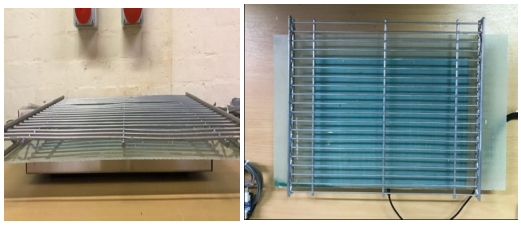

Figure 3 The drying rack

The data was collected by using a set of devices namely:

- Weighing scale: measuring the weight and calculating the drying rate.
- Stopwatch: To measure elapsed drying time.
- Thermocouple: To measure temperature inside the ceramic sample (error ± 2°C).
- Voltmeter: To measure applied voltage in the heaters.

Through the experimental setup and procedure, it was identified that the control variables (independent variables) were Voltage and Time. The dependent (response) variables were temperature (primary response) and moisture content in the sample (secondary response).

3.1 Experimentation

The control variables (X) can be correlated with response variables (Y) as shown in figure 4. The voltage supply of the heater and the running time can determine the temperature produced and thereby the drying rate. Initially, a classification experiment was performed with altering voltage and time in 8 trials. These tests enabled the prediction of the levels of both these factors that can result in 5% moisture reduction.

The responses could be measured in a quantitative manner utilising the data collection mechanisms discussed earlier. However, the irregular lab ambient microclimate introduced additional variables which could not be readily controlled. These noise variables (Z) could lead to discrepancies in the measured responses and debase the results. Therefore, an insulating Celotex chamber, shown in figure 5, was built to minimise the variation in the environment in which the experiments were being conducted. The other noise factor observed was the lid starting weight which depended on the casted lid model as well as the starting moisture content and it is believed that it may have introduced some variations in the results.

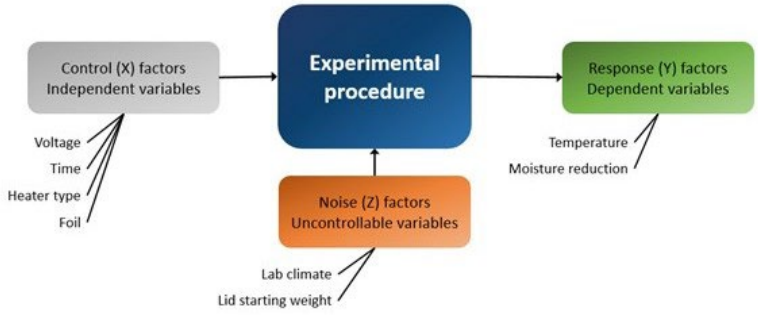

Figure 4 Relation between response variables and control variables

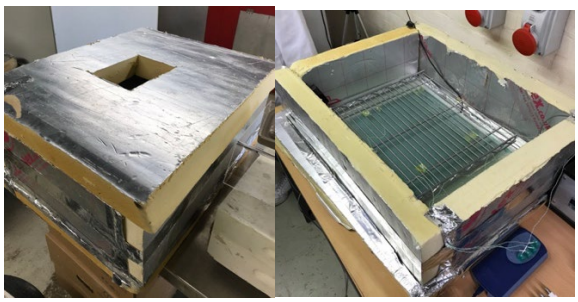

Figure 5 Celotex chamber

4. Results and discussion

Firstly, the heater was set to the appointed voltages to allow for measuring the temperatures produced at its surface. It was observed that the temperature is proportional to the voltage supply as seen in figure 6. It is important to note that the heater took around 5 minutes for the heater to reach a stable temperature and hence 5 minutes were allowed to elapse before a lid was placed underneath it.

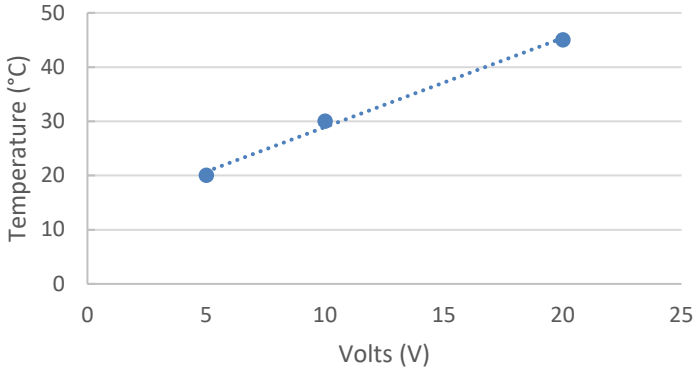

Figure 6 Supplied voltage and the corresponding temperature

4.1 Initial experiments

After identifying the generated temperatures, green body lids were heated according to the approach presented in section 3. The results are shown in figure 7. It can be observed that that the weight reduction follows a similar trend for the three applied voltage levels but the rate at which the weight reduces was faster for higher voltages. While 20V provided the most uniform reduction, 55 minutes were not enough to achieve the desired 5% reduction. Therefore, the higher the measured temperature, the higher the reduction in weight over the same period. This can be attributed to the Infrared active water molecules [17] which evaporates at a higher rate when exposed to more IR energy.

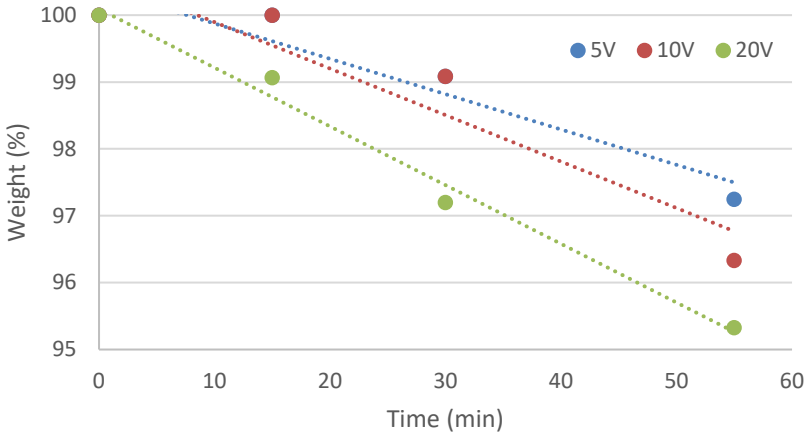

Figure 7 CNTG classification experiments results

4.2 Comparative and penetrative testing

In order to appropriately compare the two heaters, both their surface temperatures were set to 45°C and the heating was left to take place for 55 minutes. As seen from figure 8, both heaters did not start with the same rate of drying as the silicon heater took longer to reduce the weight of the green body initially. This indicates that the radiation-emitting proficiency of the CNTG heater surpasses that of the Silicon heater which could be attributed to higher emissivity.

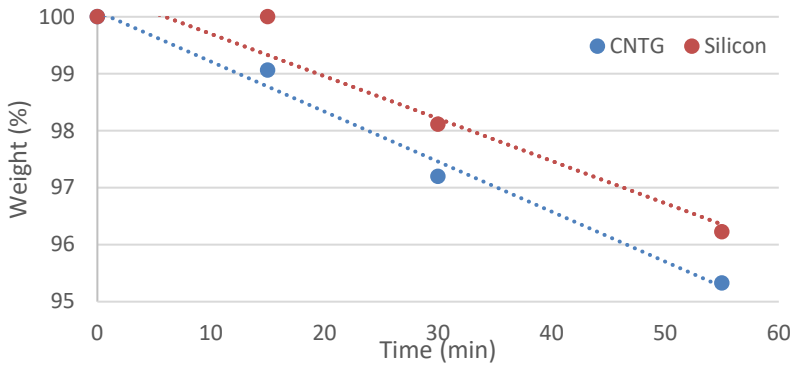

Figure 8 Weight reduction of CNTG and silicon heater

The energy efficiency of an infrared dryer relates directly to the power required to produce a specific amount of heat [20]. Hence, to further compare the heaters, the power used to produce the same surface temperature was identified by determining the voltage and current supplied to them. The results show that the Silicon heater requires 4 times more power to generate matching temperatures (267W for silicon and 65 for CNTG). This makes the CNTG heater ideal to be used in an industrial setting where minimising the energy running costs is essential.

After demonstrating that utilizing IR can indeed remove moisture from the ceramic green body, its penetrative ability was established by embedding 4 thermocouples in a parallel-line spaced configuration inside the green body where temperature readings were collected every 1 minute for an hour. The results are shown in figure 9. It is apparent that the energy produced by IR is capable of penetrating through the lid as the temperature rise was both immediate and simultaneous at the 4 points with minor variations.

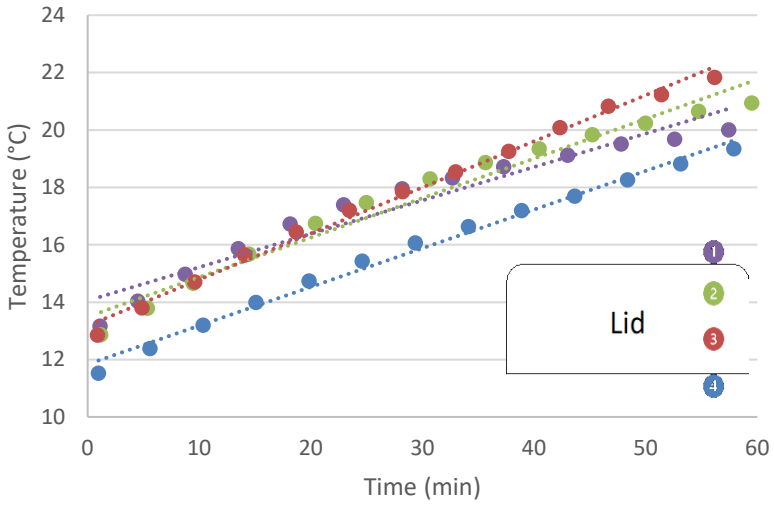

Figure 9 Buried thermocouples results

4.3 IR Reflective testing

As conferred earlier, heat losses may occur due to the reflection of a fraction of the IR rays from the surface of the sample. Therefore, introducing aluminium foil could act as a radiant barrier reducing the heat loss significantly by reflecting the rays back onto the ceramic sample. Consequently, to inspect such attribute, firstly, a rectangular piece of aluminium foil was placed on the non-heating sides of the heater and then on all the heater's outer surface where the CNTG was sprayed, and the results were compared. Figure 10 shows that the weight reduction in both configurations was similar for the first 15 mins. However, as time passed, some changes started to appear on the heater with foil only in the sides, which showed a significant reduction of 5.46% compared to 3.81% with the foil placed all around. While the result proves that radiant heat could be reflected and directed, having the foil on the heating section of the heater may have caused some heat dissipation via conduction and therefore less heat is reaching the sample.

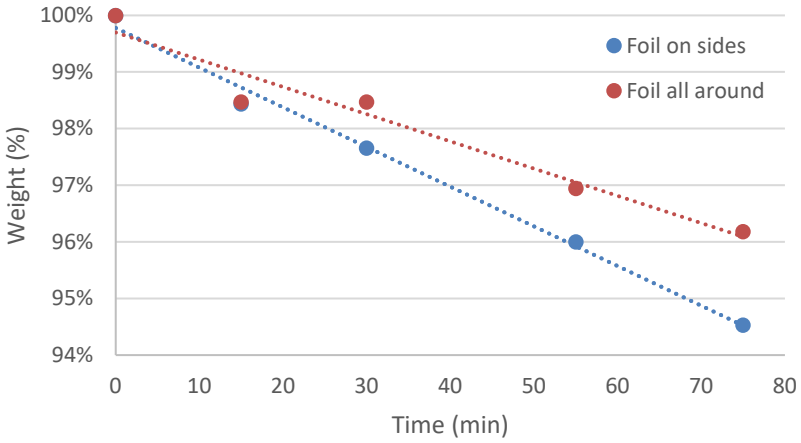

Figure 10 IR reflective testing with aluminium foil

5. Conclusion

The project was established to examine the viability of utilising CNTG as an emitter of LWIR for pre-drying ceramics and the possibility of deploying it in a manufacturing setup. The science concerning the behaviour of ceramics while drying and the principal characteristics that influence IR emittance was investigated to aid the justification of using CNTG. The experiments conducted in the research allowed for the recognition of the CNTG heater's ability to not only dry the ceramic green bodies in a uniform and homogeneous manner but also reduce the time needed for the process. This was presented by successfully reaching 5% reduction in weight of the ceramic green body. Moreover, it provided an insight into the radiant emittance and power efficiency of CNTG in such application. The ability to spray paint CNTG on any surface makes it highly versatile and therefore could be utilised to produce custom heaters of various shapes and sizes to irradiate every section of the complex contours of different ceramics products.

Cracking is one of the most common defect in ceramics production [21]. Consequently, reducing production losses that are caused by cracking at the pre-drying stage can lead to substantial financial savings as it will decrease the amount of rejected products that would need to be recycled or remanufactured. Therefore, a project to industrialise the findings may be compelling. On that account, the experiments could be repeated by building on the findings with 4 control variables full factorial experimental design in a randomised fashion at the factory floor. Moreover, as expressed in the literature review, 6 µm is one of the wavelengths at which the water molecule bends resulting in the release of the Van Der Waals forces and allowing water to change phase from liquid to gas. According to Winn's displacement law, it was estimated that the CNTG heater produced IR with a peak wavelength of 9 µm. However, it would be immensely beneficial to be able to accurately identify the wavelength produced using a spectrometer. Further work could aim to classify the varying power input and the corresponding IR wavelengths generated as well as including varying thickness of the sprayed CNTG as a factor for heater design optimization.

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