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High-Throughput Method to Predict Extrusion Pressure of Ceramic Pastes

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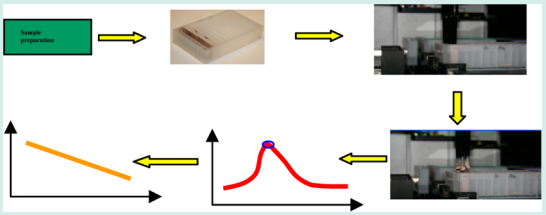
ABSTRACT: A new method was developed to measure the rheology of extrudable ceramic pastes using a Hamilton MicroLab Star liquid handler. The Hamilton instrument, normally used for high throughput liquid processing, was expanded to function as a low pressure capillary rheometer. Diluted ceramic pastes were forced through the modified pipettes, which produced pressure drop data that was converted to standard rheology data. A known ceramic paste containing cellulose ether was made and diluted to various concentrations in water. The most dilute paste samples were tested in the Hamilton instrument and the more typical, highly concentrated, ceramic paste were tested with a hydraulic ram extruder fitted with a capillary die and pressure measurement system. The rheology data from this study indicates that the dilute high throughput method using the Hamilton instrument correlates to, and can predict, the rheology of concentrated ceramic pastes normally used in ceramic extrusion production processes.



KEYWORDS: *extrusion, injection molding, powder chemical preparation, suspensions, auto honeycomb*

1. INTRODUCTION

The extrusion of aqueous based ceramic pastes, which is a kind of non-Newtonian fluid, into advanced ceramic parts, such as auto honeycombs, has been widely practiced in industry for many years.[1] A typical ceramic paste is mainly composed of rod-like ceramic particles with the particle size in the range 1−10 μm^2, water, and additives, including binders and plasticizers. The need to include these ingredients arises from the fact that the powders usually form agglomerates of a nonhomogeneous nature and do not produce a coherent dispersed mass that is suitable for useful processing. Therefore, a liquid (water), which functions as a continuous medium, is a necessary component and provides both a vehicle to homogenize the particles and also the medium to incorporate the necessary processing aids, such as the binders, etc. Additionally, a paste that contains ceramic powder and water alone will have three significant practical problems. First, the particles will not be homogenized because van der Waals attractive forces will cause the aggregation of the particles, and second, such a paste will normally "dewater" or phase-separate during many extrusion processes. This latter effect arises because the liquid phase (water) may migrate significantly more rapidly than the dispersed phase (powder) under the application of a pressure gradient. The result is that the paste becomes drier and as a consequence the extrusion pressure rises and eventually the paste becomes nonextrudable. Finally, ceramic powders cannot always be effectively extruded if there is only water in the paste, as they offer a very high friction at the interface of the bulk material and the processing engine (e.g., extrude). To overcome the these problems, the rheology of the water is modified by water-soluble cellulose ethers, which have been used for many years as binders providing water-retention, lubrication, and plasticization during the extrusion of ceramic auto honeycombs.[3,4]

From the manufacturer perspective, the manufacturing of these various ceramic shapes can be optimized by maximizing extrusion rate and the wet strength of the ceramic part immediately post extrusion. The extrusion rate is maximized by reducing the pressure drop across the shape forming die, and wet strength is also enhanced by the choice of added extrusion aids such as plasticizers, surfactants, lubricants and binders.[5]

There are ongoing efforts to study the relationship of the various additives in ceramic paste formulations and the effects these additives have on both pressure drop under the shear rate from 50−800 $s^{-1}$and extrudate wet strength. Specifically, it is relevant to know how these parameters are affected by the amount and type of cellulose ether in the paste formulation.[6,7] It is desired to screen the multitude of cellulose ethers available from multiple manufacturers to determine the effect on pressure drop and wet strength. However, screening these cellulose ethers at production scale is too resource intensive to be practical. Although there are some commercially available high throughput rheometers, generally called Automatic Rheometer Systems (ASCs), they are not amenable to the characterization of ceramic pastes. This is because the abrasive nature of the inorganic cordierite in the paste would negatively impact the commercially available rheometers. For example, the paste can abrade the wall of the capillary rheometer altering its surface. As a result, over time, the measurement results may become eroneous. Therefore it was

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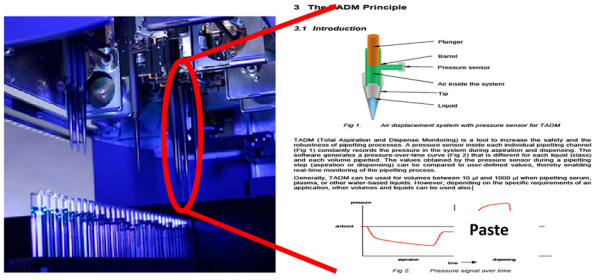
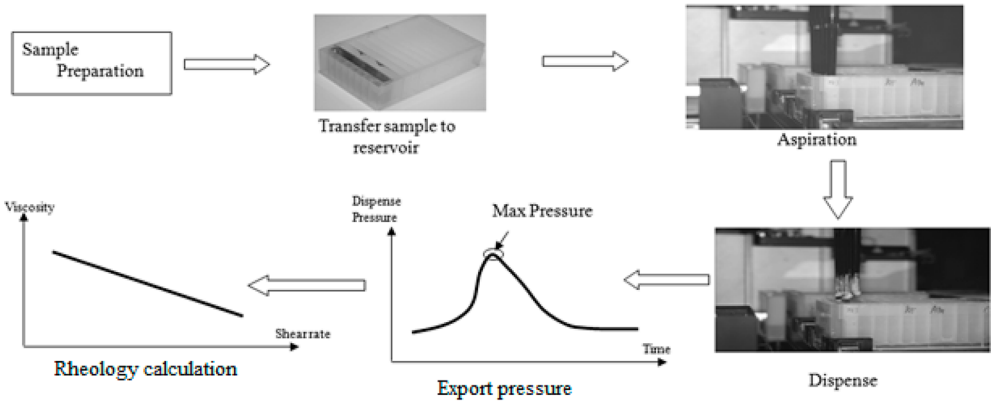
(a) Hamilton™ MicroLab Star liquid handler



(b) Pipette of Hamilton™



(c) Flow Chart of Measuring Rheology of Auto Honeycomb Extrusion

Figure 1. Schematic design method to measure rheology of auto honeycomb extrusion.

decided to explore a method that enables efficient testing of a large number of cellulose ethers affecting the extrusion pressure drop of ceramic paste using a disposable capillary. This paper describes the development of a novel high throughput research method to predict the pressure drop of typical auto honeycomb ceramic extrusion pastes.

2. MATERIALS AND METHODS

2.1. High-Throughput Method. Figure 1 shows the schematic design method to measure rheology of auto honeycomb extrusion. Figure 1a shows the Hamilton MicroLab Star liquid handler; Figure 1b shows the pipet and its internal structure. The pipet is an analog to a capillary tube in a capillary rheometer. From Figure 1b, one can seen that a pressure sensor inside each individual pipetting channel constantly records the pressure in the system during aspiration and dispensing. The software generates a pressure-overtime curve that is different for each paste and each volume pipetted. Generally, it can be used for volumes between 10 and 1000 μL when pipetting paste. Figure 1c shows the flowchart of the inventive method. The method includes 3 steps: sample preparation, measurement, and data processing. Every step will be introduced in the following sections.

2.1.1. Sample Preparation. The inorganic base used to prepare the pastes is a spray-dried cordierite body (CP 820M, Imerys Tableware, Neustadt, Germany; moisture content = 1.8%, bulk density= 996 g/L, surface area 18 m^2/g, primary particles showing 50% < 10 μm and 100% < 60 μm). Methocel A4M from The Dow Chemical Company was used as the binder, characterized by a methoxy content of 29.9% and a viscosity of a 2 wt % aqueous solution about 4170 mPa·s (Brookfield, spindle RV4, 20 rpm, 20 °C).

An aqueous solution of the binder was prepared by adding Methocel A4M to the amount of water shown in Table 1. Subsequently, the cordierite precursor powder was added followed by mixing with an overhead mixer for 50 min at 1300 rpm. The paste samples were kept in a refrigerator at 4 °C until tested, nominally 16 h (overnight).

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Table 1. Formulations for High Throughput Measurement

sample	cordierite (g)	Methocel A4M (g)	water (g)	water (%)
paste 1	100	5	328	76
paste 2	100	5	245	70
paste 3	100	5	206	66

2.1.2. Measurement. The measurement step includes three substeps: (i) transfer samples to reservoir, (ii) aspiration, and (iii) dispense. To measure the pressure drop, Hamilton high volume (1000 μL) disposable pipettes were used. The cone shaped tip of the pipet was removed to create a strait cylinder section with a radius of 2 mm. The paste does not come in contact with any other parts of the Hamilton liquid dispenser except the disposable pipet. That means the pipet can be disposed after one measurement, without any causing harm to any other part the equipment.

After storage of the paste at 4 °C, the paste was allowed to warm to room temperature for one hour. The paste was then transferred to the sample reservoir and the rheology measurement was started with the following parameter settings: (i) The pipet aspiration rate for all runs was 10 μL/s. (ii) To measure the rheology at different shear rate, the dispense rate was set as follows: 10, 50, 100, 200, 300, 400, and 500 μL/s. The shear rates could be calculated from the dispense rates through eq 3 in section 2.1.3.

2.1.3. Data Processing. The data processing step includes 2 substeps: (i) export pressure and (ii) rheology calculation. The automated Hamilton MicroLab Star instrument is equipped with eight pipet channels, each of which has a pressure sensor (see panel b in Figure 1). The operation of Hamilton instrument is based on syringe drives, which control the flow rate volumetrically for each of the pipet channels.

The various aqueous based ceramic paste formulations were mixed and loaded into a reservoir of multiple cells. The Hamilton instrument automatically aspirated each sample into the custom pipet and then dispensed the various concentrations of ceramic paste, while recording the pressure. The dispense, or extrusion pressure, data was analyzed to obtain an extrusion rheology profile based on classical rheology theory described by eqs 1−3.[8,9]

$$\tau_R = \frac{\Delta P R}{2L} \tag{1}$$

τ_R and ΔP represent the wall shear stress and maximum pressure on expel curve. The radius R of the used pipet tip was 2 mm. L represents the length of the extruded paste in the pipet. Since the discharge volume is set 200 μL, L can be obtained by the following equation:

$$L = \frac{\text{volume}}{\pi R^2} = \frac{200}{3.14 \times 2^2} = 15.92 \text{ mm} \tag{2}$$

Using the Weissenberg−Rabinowitsch correction the shear rate ($\dot{\gamma}_R$) can be calculated according to eq 3

$$\dot{\gamma}_R = \frac{Q}{\pi R^3}\left[3 + \frac{\mathrm{d}\ln\left(\frac{Q}{\pi R^3}\right)}{\mathrm{id}\ln \tau_R}\right] \tag{3}$$

where Q is the dispense rate (μL/s).

The term $d\ln(Q/\pi R^3)/(d\ln\tau_R)$ is the slope of line in Figure 2[8] that shows the shear rate ($\dot{\gamma}_R$) as a function of the wall shear stress τ_R.

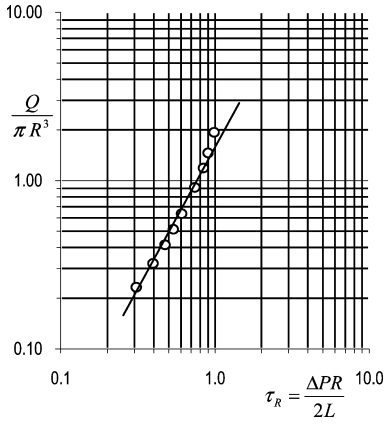

Figure 2. Weissenberg−Rabinowitsch Correction.

Application of eqs 1 and 3 in eq 4 provides the viscosity ($\eta(\dot{\gamma}_R)$) with Weissenberg−Rabinowitsch correction.

$$\eta(\dot{\gamma}_R) = \frac{\tau_R}{\dot{\gamma}_R} \tag{4}$$

Similar calculations were completed for data gathered on the highly viscous paste samples tested on the hydraulic ram extruder in the section 2.2, where volume extrusion rate and capillary diameter is known. Pressure drops were recorded at various volume flow rates with the hydraulic ram extruder.

2.2. Ram Extruder Experiments. Extrusion experiments with various amounts of water content were conducted on a Händle 5 cm diameter hydraulic ram extruder. The formulations (green bodies 1 and 2 in Table 2) have solids loadings similar to typical commercial ceramic pastes. A third sample, with slightly higher water content (validation green body in Table 2), was extruded through the same process to provide an additional data point to validate the final high throughput model.

Table 2. Green Body Formulation for Extruder Tests

sample	cordierite (g)	Methocel A4M (g)	water (g)	water (%)
green body 1	100	5	36.3	26
green body 2	100	5	28	21
validation green body	100	5	54.7	34

The pastes were mixed for each formulation in a mortar and pestle at room temperature, then placed into the extruder barrel and extruded through a 5.3 mm diameter die (L/D = 3.3) at a constant rate of 5 cm/s and repeated twice to ensure a homogeneous mixture. This paste was then reloaded into the ram extruder and forced through the same die. Pressure drops were recorded continuously while varying the extrusion rate. All mixing and extrusion pressure tests were completed at room temperature (22 ± 2 °C). All components of the paste, binder, and cordierite body, were the same as those used in the high throughput experiments. The speed and pressure drop data were used to calculate apparent viscosity versus apparent shear strain rate in the following sections.

3. RESULTS AND DISCUSSION

3.1. Paste Rheology Profile. The viscosity of the paste strongly depends on the applied shear rate and amount of water

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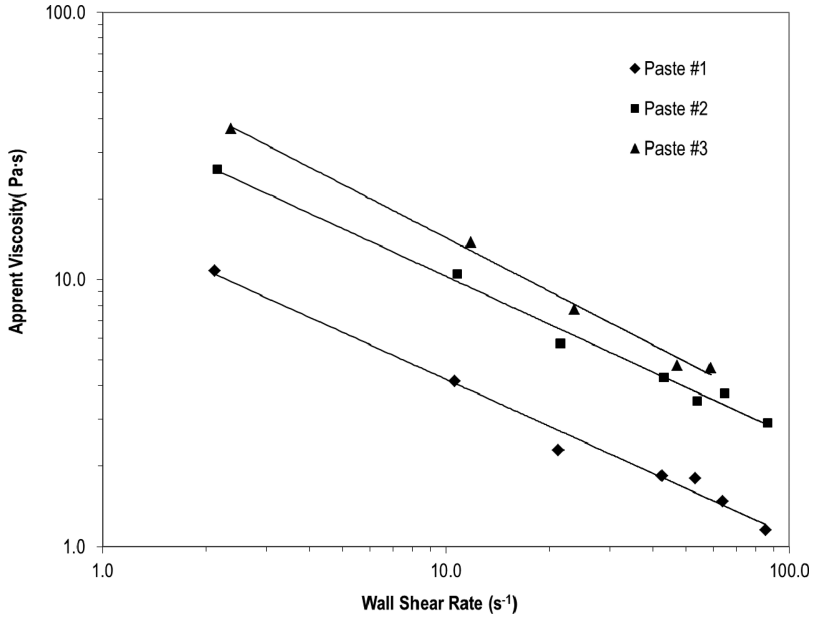

Figure 3. Apparent viscosity vs wall shear rate of high throughput data at room-temperature for paste formulations as shown in Table 1

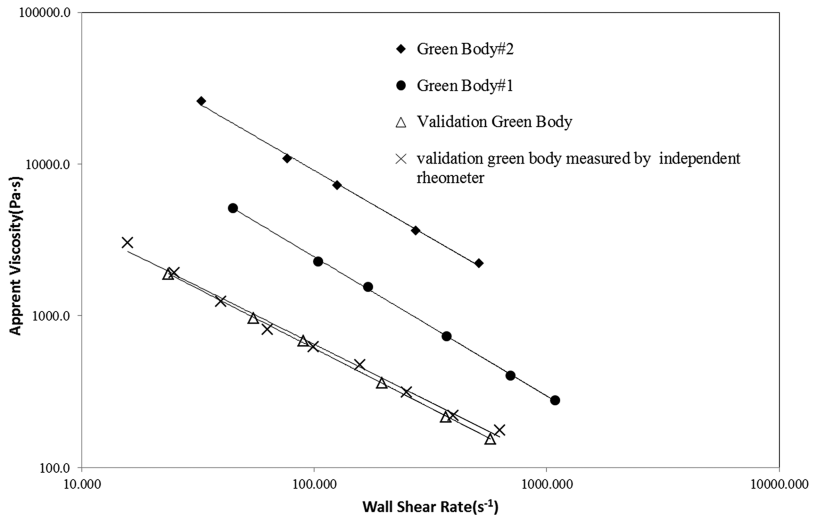

Figure 4. Apparent viscosity vs wall shear rate for hydraulic ram extrusion at room-temperature for paste compositions as shown in Table 2

Table 3. Correlation of Shear Rate and Viscosity in Figures 3 and 4

sample	water loading (g)	equation	R^2
paste 1	328	$y = 16.215x^{-0.584}$	0.9861
paste 2	245	$y = 40.231x^{-0.594}$	0.9905
paste 3	206	$y = 66.075x^{-0.665}$	0.9948
green body 1	36.3	$y = 167076x^{-0.917}$	0.9996
green body 2	28	$y = 542684x^{-0.888}$	0.9973
validation green body	54.7	$y = 22725x^{-0.786}$	0.9996
validation green body measured by independent rheometer	54.7	$y = 21920x^{-0.764}$	0.993

as shown in Figure 3 for the high throughput data and in Figure 4 for the hydraulic ram extrusion data. Table 3 summarizes the correlation equation of Figures 3 and 4. The paste viscosity decreases as shear rate increases. A higher water loading results in a lower apparent viscosity.

Table 4. Correlation of Shear Rate and Pressure in Figures 5 and 6

sample	water loading (g)	equation	R^2
paste 1	328	$y = 258.14x^{0.4158}$	0.973
paste 2	245	$y = 640.47ix^{0.4062}$	0.9799
paste 3	206	$y = 1051.9x^{0.3352}$	0.9798
green body 1	36.3	$y = 1891423x^{0.083}$	0.953
green body 2	28	$y = 5594238x^{0.129}$	0.945
validation green body	54.7	$y = 257262x^{0.214}$	0.995

With both the high throughput results and the ram extrusion results, the pressure increases with increasing shear rate as shown in Figures 5 and 6. Table 4 summarizes the correlation equation of Figures 5 and 6.

3.2. Water Loading Dependence and Extrapolation. The dependence of viscosity and pressure on the applied shear rate can be expressed as shown in eqs 5 and 6. Therein, η, P, and $\dot{\gamma}$ are the viscosity (Pa s), extrusion pressure (Pa), and

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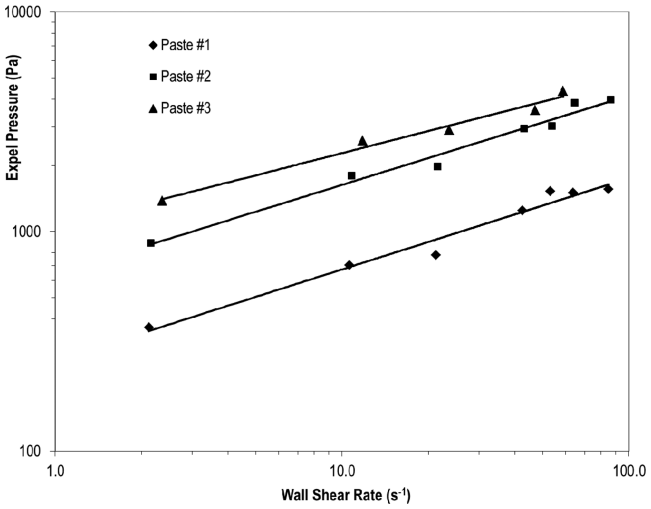

Figure 5. High-throughput extrusion pressure vs wall shear rate at room-temperature for paste compositions as shown in Table 1

shear rate (s^{-1}), respectively. k, n, m, and t are model parameters.

$$\eta = k\dot{\gamma}^{-n} \quad (5)$$

$$P = m\dot{\gamma}^{t} \quad (6)$$

In Figures 3−6, it is apparent that the slope and the exponent are dependent on the water loading. Table 5 summarizes the water-loading dependence of the rheology model.

Figure 7 shows all k and m values of Table 5 as a function of the water loading. In Figure 8, the n and t values of Table 5 are plotted against the water loading. On the basis of the study of both figures, it can be seen that the high viscosity of the more typical ceramic pastes measured with a ram capillary system can be predicted by extrapolation of the less viscous paste data run in the Hamilton high-throughout system.

3.3. Validation. In this work, the correlation between highthroughput and ram extrusion pressure was established on the basis of the data generated using the samples shown in Tables 1 and 2. To further validate the correlation, a third sample, with a water content between those of samples tested with the high-throughput instrument and the ram extrusion system (validation green body in Table 2), was tested with the ram extruder. The rheology profile for this validation sample is shown in Figures 4 and 6 The resulting rheology model parameters are summarized in Tables 3−5. Figures 7 and 8 show how well the parameters for the validation green body sample fit into the established correlation between the high-throughput dilute paste and the typical ceramic extrusion formulation.

We also used an independent rheometer to measure the viscosity at different shear rate for validation sample. The rheometer is ARES-G2 rotary rheometer manufactured by TA Instruments Company. The plate gap is about 1 mm and plate diameter is 25 mm. The results are plotted in Figure 4. It can be seen that the regression line obtained from the independent rheometer approaches that obtained from hydraulic ram extrusion very closely.

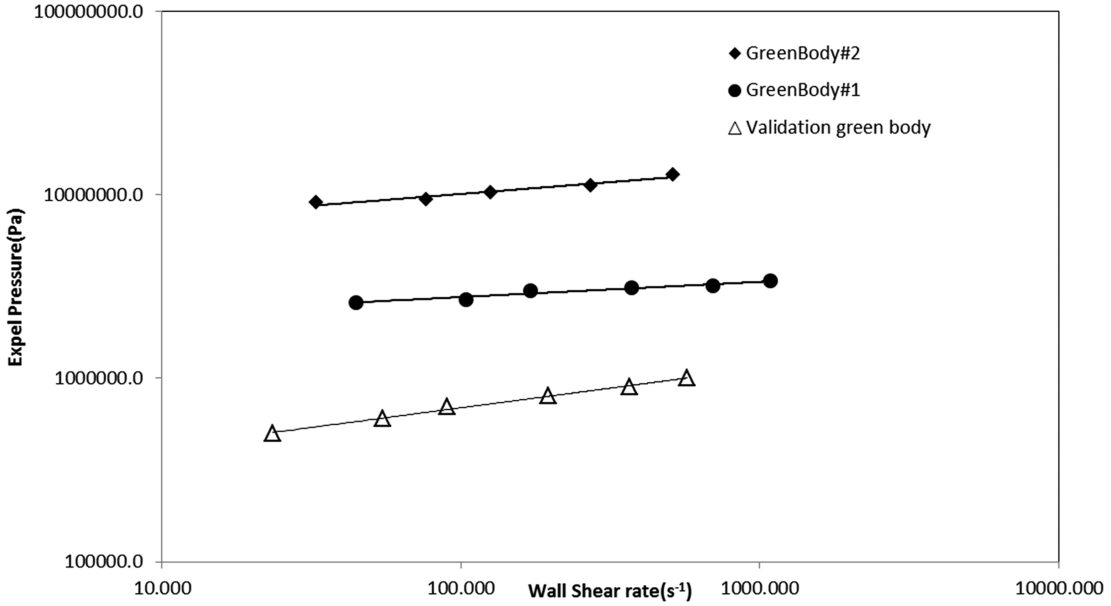

Figure 6. Ram extrusion pressure vs wall shear rate at room-temperature for paste compositions as shown in Table 2

Table 5. Parameters in Rheology Model

sample	water loading (g)	k	n	m	t
paste 1	328	16.215	0.5842	258.14	0.4158
paste 2	245	40.231	0.5938	640.47	0.4062
paste 3	206	66.075	0.6648	1051.9	0.3352
green body 1	36.3	167 076	0.917	2 000 000	0.083
green body 2	28	542 684	0.888	6 000 000	0.1287
validation green body	54.7	22 725	0.786	257 262	0.2143

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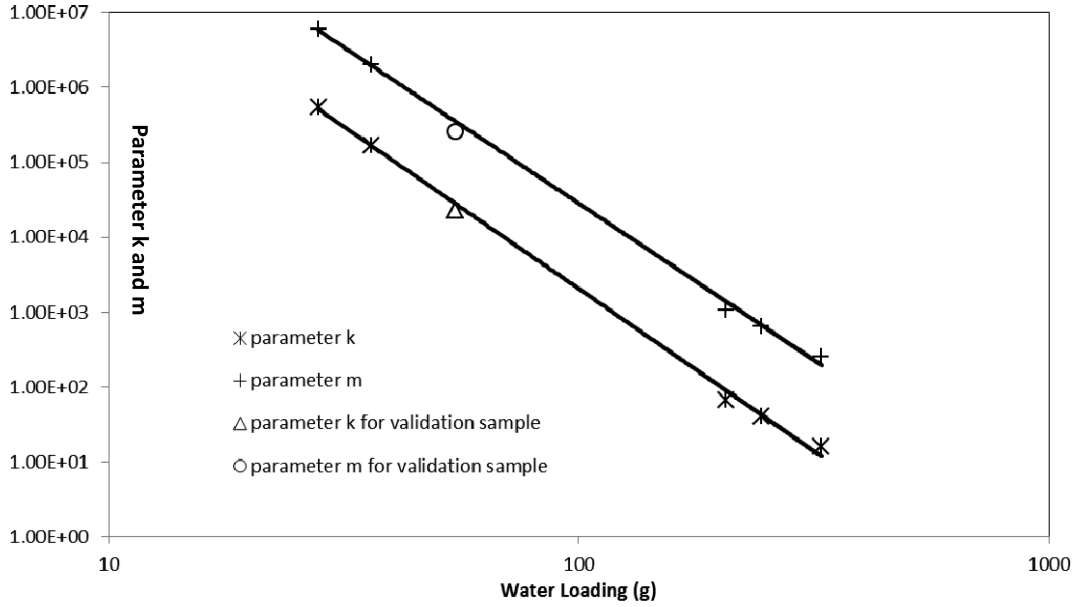

Figure 7. Parameters *k* and *m* of the rheology models 5 and 6 as a function of the water loading for ram extrusion paste samples and high-throughput paste samples.

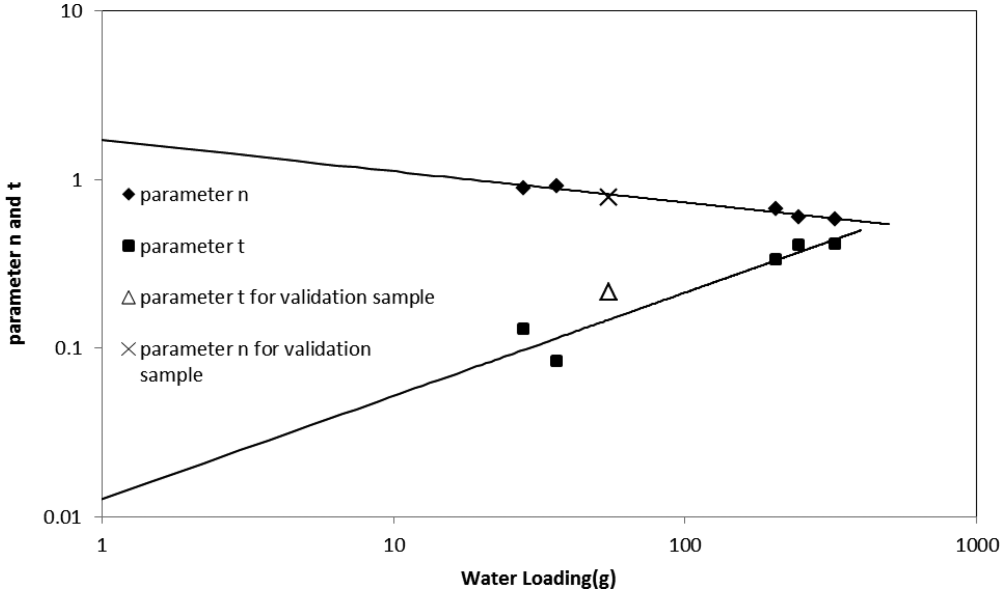

Figure 8. Parameters *n* and *t* of the rheology models 5 and 6 as a function of the water loading for ram extruded paste and the high-throughput paste.

4. CONCLUSIONS

For screening and formulation development purposes, typical production-sized paste extruders are inefficient because of the large amount of raw material and time needed to evaluate performance. Smaller extrusion equipment can both reduce the material costs and speed up paste formulation development. However, even using the smaller lab-scale hydraulic ram extrusion equipment, as used in this study to confirm the high-throughput method, can be very time and material intensive. For example, turn around time with this 5 cm ram extruder, including sample mixing, pressure data collection, and cleaning, can take around 45 min per sample.

The Hamilton MicroLab Star instrument was able to function as a low pressure capillary rheometer for diluted ceramic pastes. The rheology data for the diluted pastes correlate well with rheology data generated with a hydraulic ram extruder using pastes of higher, more typical, viscosities and can be used to predict the pressure drop of typical ceramic pastes used to make auto honeycombs. This high-throughput method enables higher sample screening rates for paste additives. The advantage of this newly developed high throughput method is that it requires very small amounts of polymer binders (0.05 g per trial) and with a cycle time of one minute per sample is very fast. Therefore, this high-throughput system, or a similar system, is an ideal tool to screen new binders, lubricants, and additives in ceramic paste formulations.

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Notes
The authors declare no competing financial interest.

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