RHEOLOGY AND PROCESSING OF COARSE GRAINED SUSPENSIONS FOR PRESSURE SLIP CASTING OF GRADED COMPOSITES BASED ON REFRACTORIES

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ABSTRACT

This contribution investigates the pressure slip casting and rheological behavior of coarse grained slips of three different particle sizes. Using these coarse grained slips the processing of graded composites for refractory applications was studied. For the pressure slip casting, a pressure filtration cell which uses pressurized air for the filtration was applied. To investigate the rheology of the slips, an adapted falling sphere viscosimeter was used.

After optimizing the filtration behavior, the surface quality and the bonding of the different filter cake layers as well as the thixotropic behavior of the slips, a refractory composite with three layers without macroscopic cracks was succesfully manufactured. The bonding between the filter cake layers showed no delamination and the excellent bonding even remained after thermal shock.

Keywords: Pressure slip casting, composites, rheology, thermal shock, X-ray computed tomography

INTRODUCTION

Slip casting is one of the fundamental forming techniques for ceramic products. For slip casting, the preparation of a stable suspension (slip) with a sufficient low viscosity is necessary as a first step. This slip is then filled into a porous mold and a green ceramic body builds up due to cake filtration. The green ceramic body is then dried and fired, which eventually results in a final ceramic body.

During conventional slip casting the driving force for the filtration is capillary suction induced by small pores in the molds made of plaster of Paris. Since the newly formed ceramic body acts as a additional filtration medium for the following filtration cake layers, the filtration time increases as a qudratic function of the filter cake thickness. Thus, the filtration time becomes exceedingly long with higher filter cake thicknesses. Consequently, slip casting is especially profitable for thin walled and complicated shapes.

To speed up the filtration time, an external pressure can be either applied on the slip side or on the mold side, which results in the pressure slip casting technique. Pressure slip casting has especially the advantage that more durable polymer molds can be used instead of plaster of Paris molds. Furthermore, compaired to conventional slip casting, it is not necessary to dry polymer molds and pressure slip casting also allows a high degree of automation.

Conventional and pressure slip casting also allow the manufacturing of graded composites. By changing the slip composition discrete or continuous gradients can be achieved. These graded composites can consist of layers of differing material compositions as well as of layers with other differing characteristics such as porosity.

Recently, pressure slip casting was also presented for coarse grained oxide ceramics which can be used for refractory applications.[1] In order to implement the pressure slip casting of coarse grained ceramics it was first necessary to develop a stable slip. This stabilization was achieved by using a binder system based on hydrocolloids such as xanthan and guar gum.

Additionally, pressure slip casting was further developed and coarse grained composites consisting of two layers with a different maximum particle size were achieved. This research was then extended to graded composites with three layers having a maximum grain size of 3 mm, 1 mm and 0.5 mm, respectively. However, the composites with three layers still contained some cracks.[2] Furthermore, in order to upscale the pressure slip casting of coarse grained composites, an understanding and optimization of the rheological characteristics of the used slips is necessary.

Consequently, this study will present an optimized processing of graded composites with three layers and the investigation of the thixotropy of the slips using an adapted falling sphere viscosimeter.

EXPERIMENTAL

The aim of the present study was to investigate the effects of several processing factors on the filtration of coarse grained slips and to obtain crackfree graded composites with three layers. A second aspect was the investigation of the thixotropy of the used slips using an adapted falling sphere viscosimeter.

In all experiments several grain size fractions of alumina rich magnesium aluminate spinel with a maximum grain size of up to 3 mm were used. Moreover, reactive alumina was used for the finest particle fraction. To prevent sedimentation of the slips, a water-based solution of xanthan and guar gum was added. During slip casting the water content of this solution is reduced due to filtration, whereas the xanthan and guar gum remain in the ceramic body. Thus, this reduced water content causes a remarkable viscosity increase of the xanthan/guar gum solution, which then acts as a binder during pressure slip casting. Furthermore, citric acid was added as a dispersant because in a previous study it was shown that citric acid results in a better filtration behavior than a dispersant based on a polymerization product of polyethylene glycol, which is often used for refractory castables.[2]

All slips were prepared in a standard mortar mixer. Before the beginning the xanthan/gum solution was carefully prepared to avoid lump formation of the xanthan and guar gum. During the slip preparation all particle fractions and the dispersant were first dry mixed. Then the binder solution was added in three steps. After each consecutive binder addition and stirring, the mixing vessel was carefully scrapped to ensure a homogeneous mixture. To adjust the workability, a final amount of water was added at the end before the mixture was stirred for a last time.

For the filtration experiments a pressure filtration cell was used, which is in principle a sealed tube with a inner diameter of 66 mm. At the bottom of the pressure filtration cell a polymer mold made of PMMA was mounted. To optimize the filtration of the slips, a slip amount reaching exactly 200 g was filled into the pressure filtration cell. The filtration cell was then sealed and pressurized air was applied from the top of the slips. The filtrate mass was registered by a computerized balance. To obtain graded filter cakes, a sequential filtration of the slips was applied. Consequently, first the slip with 3 mm maximum grain size (S_3) was filled into the pressure filtration with a weight of 200 g, which was then filtrated. Then the following slips (S_1 and $S_{0.5}$, respectively) with a weight of 100 g and 50 g, respectively, were sequentially filtrated on top of the previous filter cake. The filtration of each filter cake layer was optimized so that a thin layer of unfiltrated slip remained on top of the filter cake in order to improve the bonding with the next filter cake layer. A scheme of a graded filter cake with two layers is given in Fig. 1.

To optimize the filtration and processing of the slips, the particle size distribution and the amount of the finest particle size fraction were evaluated. All factors were investigated in full factorial experimental designs because they allow an efficient evaluation of several experimental factors as well as their interactions at the same time. To assess the effect of the investigated factors, the filter cakes were first judged regarding the surface quality, the overall quality of the filter cakes and eventually regarding the bonding of the different filter cake layers. In all cases an ordinal scale was applied.

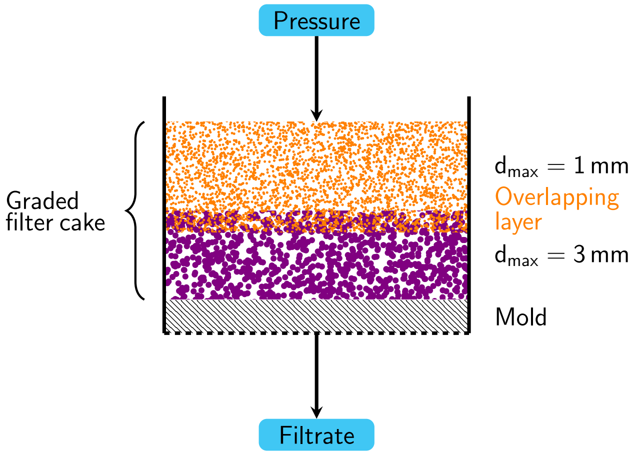


Fig. 1: Scheme of the graded filtration to manufacture graded composites for refractory applications

For the evaluation of the particle size distribution, a recently proposed particle size distribution model according to Fruhstorfer and Aneziris[3] was utilised, which is given in equation (1).

$$CPFT = \left(\frac{d}{d_{max}}\right)^{\left(n_{min} + \frac{d \cdot (n_{max} - n_{min})}{d_{max}}\right)} \qquad (1)$$

In this equation $CPFT$ is the cumulative percentage finer than a particle size d, d_{max} is the maximum particle size, n_{max} is distribution modulus at d_{max}, while n_{min} is the distribution modulus at an infinitesimal particle size.

To study the influence of the particle size distribution on the filtration behavior, n_{min} and n_{max} were varied in a small full factorial experimental design, which is given in Table 1.

Tab. 1: Slip compositions to study the influence of the particle size distribution

Raw material	$MgAl_2O_4$ and Al_2O_3			
n_{min}/n_{max}	0.28/0.4	0.3/0.4	0.28/0.6	0.3/0.6
d_{max} (mm)	3	3	3	3
Batch identifier	B_I	B_{II}	B_{III}	B_{IV}
1-3 mm (wt.%)	24	25	32	35
0.5-1 mm (wt.%)	13	15	5	8
0-0.5 mm (wt.%)	15	23	15	20
0-0.2 mm (wt.%)	9	0	9	0
0-90 µm (wt.%)	10	9	10	9
0-45 µm (wt.%)	29	28	29	28
Reactive Al_2O_3 (wt.%)	0	0	0	0
Xanthan (wt.%)	0.035	0.035	0.035	0.035
Guar gum (wt.%)	0.035	0.035	0.035	0.035
Citric acid (wt.%)	0.2	0.2	0.2	0.2
Water (wt.%)	15.5	15.5	15	15

In a further experimental series, the effect of the amount of the finest particle fraction was evaluated. For that reason, an increasing amount of the finest particle fraction (reactive alumina) was added in three levels, which is summarized in Table 2.

Tab. 2: Compositions to study the influence of the finest particle fraction

Raw material	$MgAl_2O_4$ and Al_2O_3		
n_{min}/n_{max}	0.28/0.6	0.28/0.6	0.28/0.6
d_{max} (mm)	3	3	3
Batch identifier	B_{IV}	B_V	B_{VI}
1-3 mm (wt.%)	32	32	32
0.5-1 mm (wt.%)	5	5	5
0-0.5 mm (wt.%)	15	15	15
0-0.2 mm (wt.%)	9	9	9
0-90 µm (wt.%)	10	10	10
0-45 µm (wt.%)	29	24	19
Reactive Al_2O_3 (wt.%)	0	5	10
Xanthan (wt.%)	0.035	0.035	0.035
Guar gum (wt.%)	0.035	0.035	0.035
Citric acid (wt.%)	0.2	0.2	0.2
Water (wt.%)	15	15	15

For the process optimization especially the filtration behavior was analyzed. For this analysis a standard cake filtration model according to equation (2) was applied.

$$\frac{dt}{dV} = \frac{\mu(\alpha_{av} \cdot c \cdot V + R_m)}{A^2 \cdot \Delta p} \qquad (2)$$

where t is the filtration time, V the filtrate volume, A the area of the filtration medium, μ the dynamic filtrate viscosity, α_{av} the average specific resistance of the filter cake, c the effective concentration of the solids in the slips, Δp the applied filtration pressure and R_m the resistance of the filter medium.

With the initial conditions $t = 0$ and $V = 0$ equation (2) can be integrated.

The integrated equation can be then used to evaluate the filtration resistances α_{av} and R_m by approximating the t/V vs. V data by linear regression.

Tab. 3: Slip compositions to manufacture the graded filter cakes

Raw material	$MgAl_2O_4$ and Al_2O_3		
Distribution modulus n_{min}/n_{max}	0.28/0.6	0.28/0.6	0.28/0.6
d_{max} (mm)	3	1	0.5
Batch identifier	B_{VII}	B_{VIII}	B_{IX}
1-3 mm (wt.%)	32	0	0
0.5-1 mm (wt.%)	5	25	0
0-0.5 mm (wt.%)	15	13	42
0-0.2 mm (wt.%)	9	15	0
0-90 µm (wt.%)	10	20	29
0-45 µm (wt.%)	19	10	0
0-20 µm (wt.%)	0	6	18
CL 370 (wt.%)	10	11	11
Xanthan (wt.%)	0.035	0.035	0.035
Guar gum (wt.%)	0.035	0.035	0.035
Citric acid (wt.%)	0.2	0.2	0.2
Water (wt.%)	15	16	17.5
Filtration pressure (bar)	4	5	6
Slip weight (g)	200	100	50
Abort criterion (filtrate mass in g)	4	3	4

After investigating the processing parameters of filter cakes having two filter cake layers, the fabrication of crackfree graded filter cakes with three layers was examined. For this purpose especially the filtration pressure of each filter cake layer was evaluated. The final slip compositions for the graded filter cakes as well as the filtrate mass of each filter cake layer are given in Table 3. The experiments regarding the filtration pressure are summarized in Table 4.

Tab. 4: Experimental setup to investigate the effect of the filtration pressure

Identifier	d_{max} = 3 mm (B_{VII})	d_{max} = 1 mm (B_{VIII})	d_{max} = 0.5 mm (B_{IX})
I	4 bar	5 bar	6 bar
II	5 bar	5 bar	5 bar
III	6 bar	5 bar	4 bar

The fired graded composites with three layers were evaluated before and after thermal shock by X-ray computed tomography (XCT). The voxel size after reconstruction was 46 µm. Although beam hardening occured, no regions of interest were extracted in order to obtain a full overview of the graded filter cakes.

Furthermore, to achieve a further upscaling for the pressure slip casting of graded composites, a rheological characterization of the slips was performed using an adapted falling sphere viscosimeter. This falling sphere viscosimeter was recently presented by Klippel et al.[4] The falling sphere viscosimeter records the time and path during the accelaration phase of a sphere with diameter of 30 mm in the slip. The slip was kept in a water-cooled cylinder with a diameter of 90 mm and the slip volume was always 1200 ml. The sphere fell into the slip every minute for a total of 15 min. Thereby it was possible to detect a relative time-dependency of the viscosity because usually the velocity of the sphere increased with each measurement. Before the first test run, the material was at rest for 10 min in order to minimize the influence of previous handling on the slip viscosity.

For the rheological characterization the investigated factors were the maximum grain size of the slip, the water amount, the amount of the dispersant (citric acid) and the amount of the xanthan/guar gum binder. These four factors were investigated in a full factorial 2^4 experimental design. The thixotropy was evaluated as the ratio of the time of the falling sphere to reach 50 % of the maximum falling path, which was about 20 cm, at the last measurement after 15 min relative to the one at the first measurement.

RESULTS AND DISCUSSION

During the experiments to optimize the particle size distribution, a strong interaction between the two distribution moduli n_{min} and n_{max} on the filtration resistance was observed, i.e. the effect of one of the distribution moduli depended on the level of the other distribution modulus. A probable reason was that the distribution moduli interacted regarding the particle packing and hence on the filtration behavior, while generally a higher packing density can be expected from a broader particle size distribution.

Nevertheless, the batches with the lowest determined filter cake resistance (n_{min}/n_{max} = 0.28/0.4; n_{min}/n_{max} = 0.3/0.6) resulted in filter cakes with an inferior surface. Yet, the two batches with a higher filter cake resistance (n_{min}/n_{max} = 0.3/0.4; n_{min}/n_{max} = 0.28/0.6) resulted in filter cakes with a much better surface. Consequently, all further experiments were performed with distribution moduli of n_{min}/n_{max} = 0.28/0.6 as a compromise between the filtration cake resistance and the surface of the filter cakes.

Fig. 2 shows that the higher the content of the reactive alumina in the slip, the higher was the average filter cake resistance as well as the filter medium resistance. This can be explained by the higher specific surface of the reactive alumina compared to the other particle fractions, which generally incerases the filtration resistance. Furthermore, the higher the relative content of the reactive alumina in the batch, the better was also the surface of the filter cakes. Hence, all further experiments were conducted with the batch B_{VII}, which contained 10 wt % of reactive alumina.

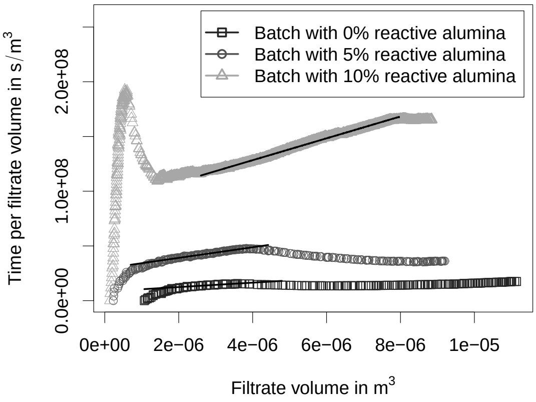


Fig. 2: The filtration curves as a function of the reactive alumina content showed an increasing filtration resistance with a higher reactive alumina content.

Fig. 3 displays the filtration curves during the fabrication of a graded filter cake. Interestingly, the filtration curves of the three filter cake layers were almost overlapping, which indicates a similar filtration behavior. In addition, a capillary dewatering stage, that is a complete filtration, was only reached during the filtration of the third filter cake layer. That means that partially some unfiltrated slip remained on the first two filter cake layers, which generally improves the bonding between the filter cake layers.[5]

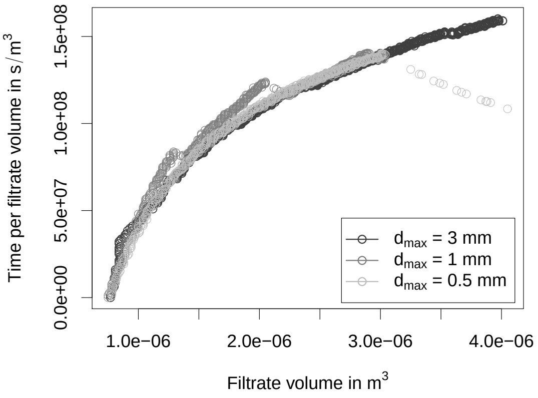
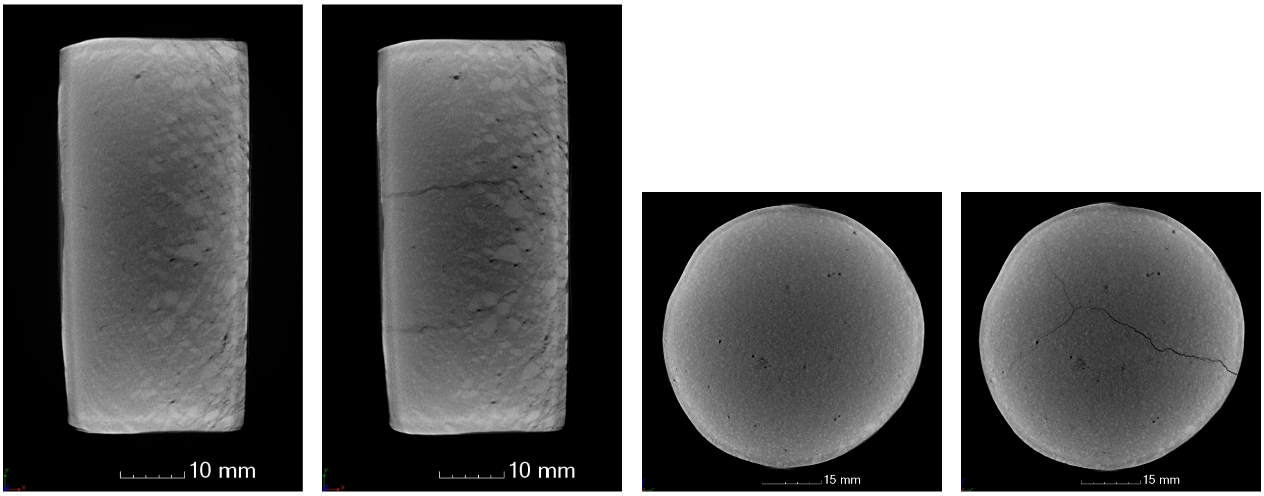


Fig. 3: The filtration curves indicate a similar filtration behavior for all three filter cake layers.

Fig. 4 displays XCT images of a graded filter cake with three layers and without macroscopic cracks before thermal shock. Moreover, an excellent bonding between the three filter cake layers and an even surface can be observed. It even seems that the filter cake layers were overlapping. An important processing factor was to ensure a partially soft layer of the first two filter cake layers in order to optimize the bonding of three different filter cake layers, see also Fig. 1 for an illustration. Additionally, it was observed that filter cakes, which were filtrated too long tended to crack during demolding. Thus, the filtrate mass of the three filter cake layers was an optimized value and is given in Table 3. Furthermore, the best results were achieved for an increasing filtration pressure with subsequent filter cake layers, which confirms the preliminary results of Schafföner et al.[5]

Furthermore, the X-ray computed tomography images in Fig. 4 also show that even after thermal shock no debonding of the filter



(a) Before thermal shock (b) After thermal shock (c) Before thermal shock (d) After thermal shock

Fig. 4: The X-ray computed tomography images indicate an excellent bonding of the layers and a homogeneous distribution of the grains in the matrix. A crack perpendicular to the filter cake layers can be observed after thermal shock.

cake layers occurred. After thermal shock a macroscopic crack perpendicular to the filter cake layers was observed, which passed through all filter cake layers.

Finally, to enable the upscaling of the whole process a better understanding of the rheological behavior is necessary. Since coarse grained suspensions are difficult to investigate with conventional rotary viscosimeters, an adapted falling sphere viscosimeter was used.

Fig. 5a) shows the path-time diagram for a slip with a high thixotropy, which was indicated by a ratio of the time of the first to the last measurement to reach the half of the height of fall. By contrary, Fig. 5b) shows a path-time diagram for a slip with a low thixotropy. Analysis of variance (ANOVA) of the factorial experimental design revealed that especially the interaction of the dispersant amount (citric acid) and the binder (xanthan/guar gum) significantly contributed to a lower thixotropy, i.e. a higher amount of the citric acid together with a lower amount of the binder xanthan/guar gum solution was benificial to achieve a lower thixotropy.

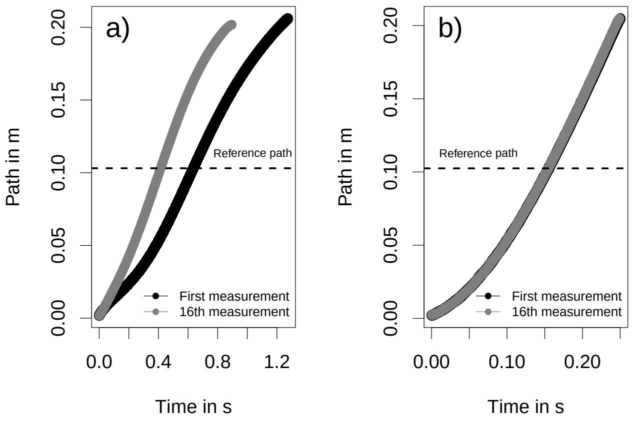


Fig. 5: Time-path diagram for slips with a high thixotropy a) and with a low thixotropy b)

The optimized processing together with the rheological characterization of the slips contribute to the upscaling of the pressure slip casting of graded composites. Results regarding the upscaling experiments will be published in a further study.

CONCLUSIONS

The current study presented the pressure slip casting of graded composites with three layers for refractory applications. For the optimization of the whole process the effects of the particle size distribution, the filtration duration, and the filtration pressure was evaluated. It was found that although an increasing amount of reactive alumina caused a longer filtration time, it was necessary to improve the surface of the ceramic bodies after filtration. Finally, a crackfree graded composite with an excellent bonding of the filter cake layers was achieved. The bonding remained superior even after thermal shock, however a macroscopic crack passing through the bonded layers was observed after thermal shock. The investigation of the thixotropy of the slips using an adapted falling sphere viscosimeter showed that especially a higher amount of citric acid (dispersant) and of the xanthan/guar gum solution, which acted as a stabilizer and binder, was benificial to reach a lower thixotropy.

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