

Effects of Changing the Specific Surface Area in the Ceramic Matrix of CAC-Containing Refractory Castables on the Dispersion and Mixing Process

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Abstract

Beside the coarse and medium grain size distribution, the matrix components play a central role in the performance of refractory castables. On the basis of practical experience, it is evident that the particle size distribution (PSD) and the resulting specific surface area of the ceramic matrix exert a significant influence on the processing, setting and sintering properties of refractory castables, which in turn influence each other. However, there is a lack of detailed highly systematic studies regarding the extent to which the properties of refractory castables are influenced by changes in the PSD or specific surface area of the raw materials in the matrix. The objective is to gain a general understanding of this.

To shed more light on this issue, the ceramic matrices were varied, resulting in model castables with gradations in the specific surface area of the matrix. The refractory castables were dispersed using three different dispersing agents with different mechanisms of action (electrosteric and steric) at graded concentrations.

The findings of this study demonstrate that refractory model castables with variations in the specific surface areas of the ceramic matrix and different dispersing agents and their concentrations necessitate substantial differences in the required mixing energy. Castables with matrices containing larger quantities of highly sintered and (very) finely ground alumina raw materials (with high specific surface areas) require less mixing energy than mixtures with lower specific surface areas. An increase of the dispersing agent content also results in a reduction in the required mixing energy and lower temperature evolution, with due consideration of the respective water content. A clear correlation can be established between the mixing energy introduced and the temperature increase during mixing. Castables with higher specific surface areas of the matrix require less mixing energy and therefore heat up less during the mixing process than castables with lower specific surface areas. The findings of the measurements of the dynamic viscosity of matrix suspensions in high shear rate ranges support these observations.

Keywords: Refractory castables, specific surface area, dispersing agents, mixing process, rheology.

I. Introduction

Refractory castables are widely used in high-temperature applications owing to their excellent thermal resistance, mechanical strength, and faster, more cost-effective and more energy-efficient installation (compared to bricklaying). These materials are typically composed of a coarse and medium grain fraction (often up to 6 mm, but also coarser grains up to e.g. 15 mm can be possible) and a fine matrix (particles < 45 µm). The distribution of raw materials in refractory castables follows multimodal packing models, where finer particles fill the pores between coarser grains, enhancing packing density and minimizing porosity^{1, 2, 3, 4}. This has led to continuous improvements in particle size reduction, with the finest materials now averaging around 0.5 µm in d_{50} ⁵. This results in an increase in

the specific surface area of the ceramic matrix of refractory castables when highly sintered and (very) finely ground alumina raw materials are used. Such refinements not only reduce porosity but also affect the processing, setting, and sintering behaviour of the castables. The influence on the dispersion and mixing process is systematically investigated in this study.

Rheological properties play a critical role in determining the workability and compaction of refractory castables. The rheology of castables is mainly defined by their matrix composition. As the particle size decreases, surface forces increase, leading to a marked rise in viscosity. Bimodal or multimodal particle distributions of the ceramic matrix have proven effective in reducing viscosity, thereby improving flowability at low shear rates. For example, bimodal reactive aluminas as common in refractory castables can optimize the flow characteristics during

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moulding^{5, 6, 7, 8, 9}. This approach can improve the flowability, enhance the overall packing density and reduce the energy required for compaction.

Despite these advances, challenges persist in optimizing flow behaviour at high shear rates, especially for modern installation methods like pumping. Dilatancy, where the viscosity increases and material stiffens while the shear rate increases, remains a significant issue in these processes. Empirical reports on pumpable castables suggest the problem of an increased resistance to flow and dilatancy in industrial applications. This depends to a large extent on the matrix formulations of refractory castables, that is if these are not properly controlled⁷. Coarse particles with irregular surface geometries can cause particle interlocking during movement, leading to increased resistance and dilatant behaviour.

In the relevant literature, many models exist to describe the relationship between the viscosity and solids content. The equation developed by Krieger and Dougherty is the most commonly used and describes the correlation of the viscosity of a suspension increasing with rising solids content^{9, 10, 11}. This can be explained by the effect that with higher packing of the particles in the system it becomes more difficult for them to move freely. The interaction between the particles increases (interparticle forces and enhanced chance of collision) and therefore the viscosity rises^{8, 9}.

The volume fraction of solid particles also affects the type of relationship between the shear rate and viscosity. With a low solids content, the suspension exhibits close to Newtonian behaviour (over a wide shear rate range). With increasing volume of the solids fraction (more particles and higher surface area per volume), shear thinning behaviour becomes more evident (high viscosity at [very] low shear rates and decreasing viscosity at elevated shear). At high solids contents, collisions between particles increase and the free movement of particles is significantly blocked. Viscosity therefore increases with shear rate and the system can behave shear thickening (dilatant) at high shear rates. At a constant proportion of solids in the suspension, the viscosity increases as the particle size decreases. Owing to a higher number of smaller particles (and a higher specific surface area), more particles interact and lead to more resistance to flow. Consequently, high solids loads of ultrafine particles lead to high viscosity levels in suspensions⁹. This could be even more pronounced at high shear rates, because the probability of a particle collision increases again due to external forces.

In general, with regard to interpreting and discussing statements and results concerning (dynamic) viscosities, it is important to note that the values for the dynamic viscosity must be considered in conjunction with the respective shear rate, as non-Newtonian flow behaviour is present in particle-loaded and concentrated suspensions.

The use of dispersing agents is essential to counteract agglomeration of the particles⁹. Dispersing agents, which are surface-active organic or inorganic molecules, play an essential role in tailoring the flow properties of refractory castables. Common dispersing agents like polycarboxylate ethers (PCE), acrylates or polyphosphates

adsorb onto particle surfaces. They cause electrostatic, steric, or electrosteric dispersion and thus prevent particle agglomeration¹². In the alkaline environment created by CA-cement, surfaces as of Al_2O_3 or SiO_2 -particles carry an overall negative charge (thermodynamic equilibrium between negative and positive charges due to protolytic reactions with the pore water and its OH^- and H_3O^+ , corresponding to a negative zeta potential in the distinct alkaline range)^{13, 14, 15, 16, 17, 18, 19}. Common dispersing agent systems exhibit a negative charge on their back bone. They therefore adsorb at the few positive partial charges on the surfaces (Ca^{2+}) and cause an increase in electrostatic repulsion due to their charge and/or steric (respectively electrosteric) repulsion due to their molecular structure^{20, 21, 22, 23}. The particles do not agglomerate and the refractory castable is in a flowable state.

An important factor in the dispersion mechanism is the interaction between dispersing agents and Ca^{2+} -ions, which are released during the dissolution of CA-cement. These ions adsorb onto particle surfaces, influencing the adsorption behaviour of the dispersing agents and, consequently, the overall rheology of the castable. More precisely, the adsorption of dispersing agents with a negative charge on negative surface groups is mediated by Ca^{2+} . This results in increased adsorption of deflocculants and the dispersion is improved²⁴.

Some dispersing agents, like polyphosphates or acrylates, precipitate with Ca^{2+} at a critical concentration (supersaturation of Ca-dispersant-compounds), leading to a disruption in the castables' flow properties and a stiffening effect^{23, 25}. Other dispersing agents, for example PCE, with long side chains, do not precipitate together with Ca^{2+} when the concentration of Ca^{2+} increases due to the dissolution of the CA-cement in the pore water. This allows the rheological system to remain stable until the point at which hydration removes water from the system^{20, 21, 23, 26}. Furthermore, hydrate phases that form can be dispersed by a significant amount of free PCE molecules in the pore water. This leads to a longer stable rheological system²³.

The balance of dispersing agent concentration and surface area is crucial, yet in practice, this is often determined empirically, leading to inadvertent overdosing or underdosing, which affects both cost efficiency and performance.

In this study, a CA-cement-based refractory model castable was modified to alter the particle size distribution and specific surface area of the matrix with the use of highly sintered, finely and very finely ground alumina raw materials. Six refractory model castables were developed with varying specific surface areas owing to differing ceramic matrix compositions. The objective was to examine how these changes affect the castables' dispersion and required mixing energy. Three different dispersing agents were added to reduce water demand while maintaining processing characteristics. The dispersing agents and their quantities were systematically varied to study their impact on matrix surfaces. Three matrix suspensions were analysed, and rheometer measurements of suspensions

with varying dispersing agents and concentrations were taken to evaluate flow behaviour at different shear rates. The dynamic viscosity values provided insight into the mixing properties of the castables, especially at higher shear rates (which corresponds to shear rates during mixing).

II. Experimental Materials and Methods

(1) Experimental materials

(a) Raw materials and their characteristics

The particle size distributions of the alumina matrix fractions were analysed using laser granulometry (Mastersizer 2000, Malvern Instruments, Malvern, United Kingdom) according to the Mie scattering measuring principle, while the specific surface areas were determined using the nitrogen adsorption method (BET) (SA-9600 Series Surface Area Analyzer, Horiba, Kyoto, Japan). The results are summarized in Table 1.

Table 1: Particle sizes and specific surface areas of the Al_2O_3 matrix components.

	RG4000	CTC20	T60/64 -45 MY LI (LI = low iron)
BET in m^2/g	6.9	1.6	0.6
d_{50} Cilas in μm	0.54	1.80	16.00

(b) Refractory castable compositions

Six self-flowing, high-alumina (Al_2O_3 raw materials supplied by Almatix GmbH, Ludwigshafen, Germany), CA-cement (Secar 71, Imerys S.A., Paris, France) containing refractory model castables with a maximum grain size of 6 mm were developed by varying the proportions of the individual ceramic Al_2O_3 components of the matrix, which differ in grain size and hence specific surface area, and/or by omitting individual components (Table 2). For an appropriate interpretation of this contribution, it must be mentioned that highly sintered and (very) finely ground alumina raw materials were used as a component of the ceramic matrix. Thus, the specific surface area of the particles only results from the (very) fine milling/grinding and not from the internal surface of weakly sintered porous alumina (like calcined alumina). Fig. 1 and Fig. 2 depict the corresponding compositions resulting from the variations in the individual matrix components (Al_2O_3 raw materials).

Three different dispersing agent systems were selected for investigation of the interaction between matrix composition (particle size distribution and specific surface area), dispersing agent and its concentration (Table 3). The corresponding concentrations of the different dispersing agents were determined by experimental means and established in preliminary tests. As polycarboxylate ether (PCE), Castament FS60 (BASF Construction Polymers GmbH, Trostberg, Germany) was chosen. Darvan 7S (Vanderbilt Minerals, LLC, Norwalk, CT, USA) was selected as polymethacrylate (PMA),

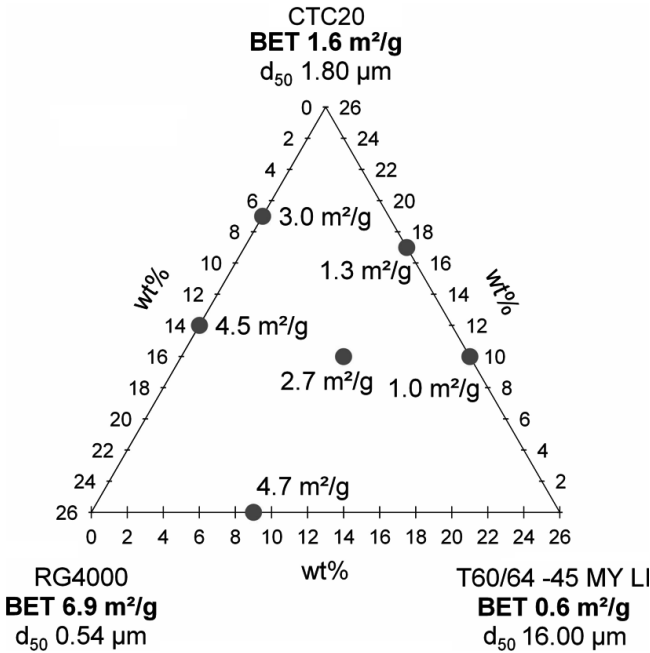


Fig. 1: Refractory model castables, shown as points in a triangular diagram with axes in wt% to illustrate the compositions of the different matrix components (Al_2O_3 raw materials) represented in the corners of the scheme.

in combination with 0.01 wt% citric acid (food grade). Sodium triphosphosphate (S-TPP) N25 – 15 (Chemische Fabrik Budenheim, Budenheim, Germany) was investigated. The S-TPP was furthermore combined with citric acid. However, the concentration of the polyphosphate was maintained at 0.05 wt%, while the proportion of citric acid was varied. The reason for that is that citric acid exhibits the stronger dispersion intensity.

The ideal water content of the model castables was determined separately for each of the three dispersing agents in preliminary flow behaviour tests. A spread-flow (according to DIN EN ISO 1927 – 4) of the multimodal distributed castables 2.7 m^2/g as a kind of reference was set at around 270 ± 20 mm. The water demand was maintained at a constant level for all model mixes with varying specific surface areas to ensure a comparability between differing matrix compositions (Table 2 and Table 3). Considering all experiments of this study, spread-flow values between 114.8 and 355.5 mm were achieved.

(c) Preparation of refractory castables

The castables (8 kg mixtures) were mixed in an intensive mixer (type R02E, Eirich GmbH & Co. KG, Hardheim, Germany). A star agitator in co-current flow was used for all experiments. Castables were mixed 1 min dry and 5 min wet after water addition with a rotation speed of 79 rpm. In order to induce the least possible mixing energy and to facilitate the observation of the greatest number of differences resulting from the different matrix compositions, the lowest adjustable speed of the agitator in the mixer was selected.

(d) Matrix suspension compositions

In order to determine the dynamic viscosity of the refractory castables developed in this study, three representative matrix suspensions were investigated.

The mixture with the lowest specific surface area ($1.0 \text{ m}^2/\text{g}$), a medium specific surface area ($2.7 \text{ m}^2/\text{g}$) and the one with the highest specific surface area ($4.7 \text{ m}^2/\text{g}$) were selected for analysis. The compositions of the matrix suspensions are presented in Table 4. The highest and lowest concentrations of the three dispersing agents employed

were considered (Table 5). In order to calculate the compositions of the suspensions, all Al_2O_3 components with a size greater than $45 \mu\text{m}$ were omitted from Table 2. Subsequently, both the raw materials (Al_2O_3 and CA-cement) and the proportions of dispersing agent and mixing water were scaled to 100 %.

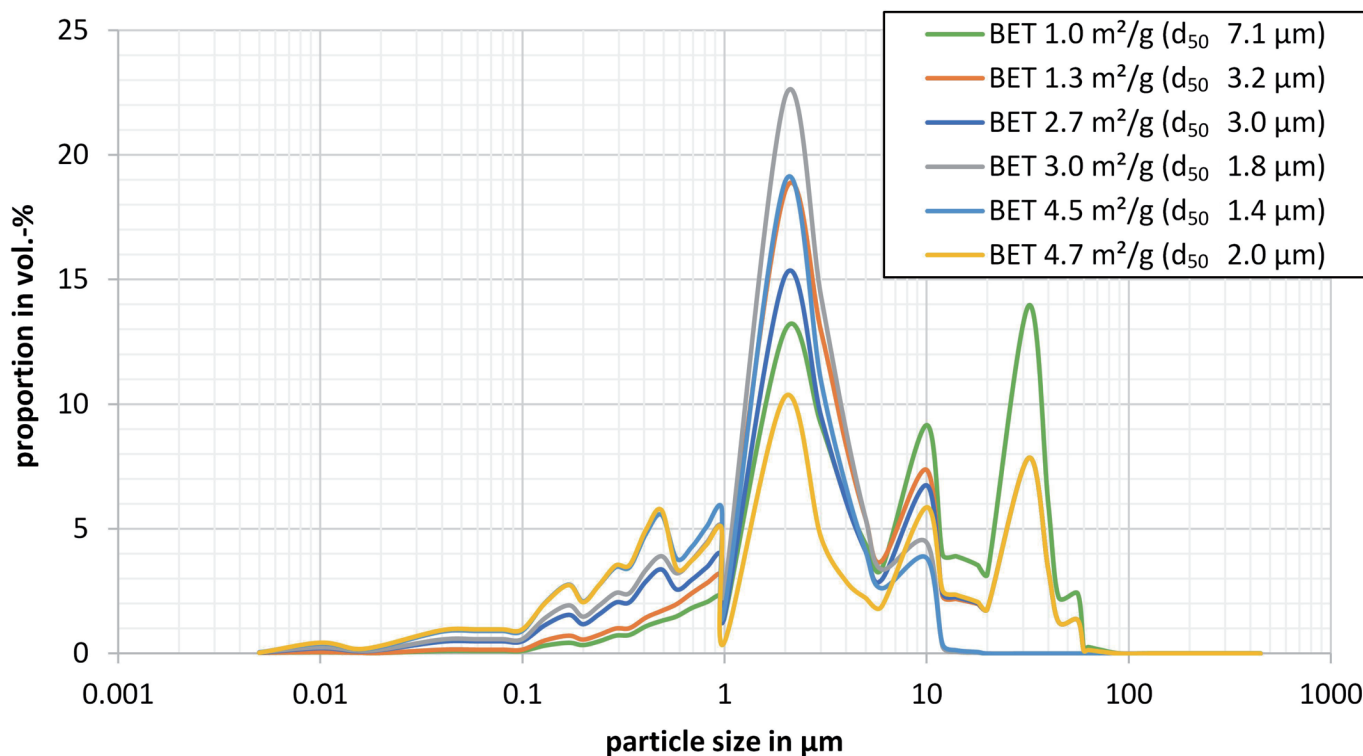


Fig. 2: Particle size distribution curves of the matrix fraction (Al_2O_3 raw materials) from the developed refractory model castables with different matrix compositions from Table 2.

Table 2: Compositions of refractory model castables with varied matrix components for different particle size distributions and specific surface areas (values for BET and d_{50} in the designation of the castables represent the matrix composition of the Al_2O_3 raw materials).

BET in m^2/g	1.0	1.3	2.7	3.0	4.5	4.7
d_{50} in μm	7.1	3.2	3.0	1.8	1.4	2.0
Component in wt%						
Al_2O_3						
T60/64 3 – 6 mm	16	16	16	16	16	16
T60/64 1 – 3 mm	21	21	21	21	21	21
T60/64 0.5 – 1 mm	11	11	11	11	11	11
T60/64 0.2 – 0.6 mm	10	10	10	10	10	10
T60/64 0 – 0.2 mm	11	11	11	11	11	11
T60/64 – 45 MY LI	16	9	9	-	-	9
Reactive alumina (CTC20)	10	17	10	19	12	-
Reactive alumina (RG4000)	-	-	7	7	14	17
CA-cement (70 wt% Al_2O_3)	5	5	5	5	5	5
Total	100	100	100	100	100	100
Water	depending on dispersing agent (Table 3)					
Dispersing agent	Table 3					

Table 3: Dispersing agents, quantities and water amount.

	Dispersing agent	Amount in wt%	Water in wt%
Polycarboxylate ether (PCE)	Castament FS60	0.075/0.10/0.15	4.8
Polymethacrylate (PMA)	Darvan 7S + Citric acid	0.07/0.10/0.13 0.01	6.3
Sodium tripolyphosphate (S-TPP)	N25 – 15 + Citric acid	0.05 0.010/0.015/0.020	6.7

Table 4: Compositions of refractory model castable matrix mixes with varied components for different particle size distributions and specific surface areas (values for BET and d_{50} in the designation of the castables represent the matrix composition of the Al_2O_3 raw materials).

BET in m^2/g	1.0	2.7	4.7
d_{50} in μm	7.1	3.0	2.0
Component in wt%			
T60/64 – 45 MY LI	51.6	29.0	29.0
Reactive alumina (CTC20)	32.3	32.3	-
Reactive alumina (RG4000)	-	22.6	54.9
CA-cement (70 wt% Al_2O_3)	16.1	16.1	16.1
Sum	100	100	100
Water	depending on dispersing agent (Table 5)		
Dispersing agent	Table 5		

Table 5: Dispersing agents, quantities and water amount.

	Dispersing agent	Amount in wt%	Designation (equivalent to real castable formulation (Table 3))	Water in wt%
Polycarboxylate ether (PCE)	Castament FS60	0.24/0.48	0.075/0.15	15.5
Polymethacrylate (PMA)	Darvan 7S + Citric acid	0.23/0.42 0.03	0.07/0.13 0.01	20.3
Sodium tripolyphosphate (S-TPP)	N25 – 15 + Citric acid	0.16 0.03/0.06	0.05 0.010/0.020	21.6

(e) Preparation of matrix suspensions

Suspensions were prepared with a hand mixer by dispersing the dispersing agents in water, and subsequently adding the dry premixed Al_2O_3 components. Finally, the cement was incorporated into the suspension, which was then homogenized. The total mixing time was approximately 5 min, which is comparable to the wet mixing time of the actual refractory castables.

(2) Experimental methods

Measurements of the dynamic viscosity of the matrix suspensions of the developed refractory model castables were carried out using a rheometer (Haake Mars 40 Rheometer, Thermo Fisher Scientific, Germany). A coaxial cylinder system (CCB25 DIN/Ti) was used as the measuring geometry. The measurement program was designed as a

step function. A shear range of 10 to 1000 s^{-1} was selected. This comprised 25 measurement steps. Each shear rate step was held for 20 s and the measured value was recorded at equilibrium. The measurements were performed using a temperature control unit at 20 °C. A longer measurement and stabilization time of the suspension should be avoided in order to avoid initial stiffening during the measurement and thus falsifying the values. For an accurate interpretation of the results, the opposite case should also be considered that the suspensions could disperse over the measurement time.

The power consumption of the mixer for calculating the required mixing energy and the temperature evolution of the mass during the mixing process were recorded continuously. The maximum values of the measured power consumption were considered in order to determine differ-

ences in the energy required during mixing of individual castable formulations. In order to be able to compare all the mixtures more clearly, the mixing energy over the total mixing time was calculated based on numerical integration of the measured respective power consumption.

III. Results and Discussion

(1) Dynamic viscosity of matrix suspensions

PCE (Castament FS60)

In Fig. 3 the dynamic viscosity measurements of matrix suspensions dispersed with PCE (Castament FS60) can be seen:

- The matrix suspensions with a specific surface area of $1.0 \text{ m}^2/\text{g}$ resulted in values of up to 2.44 (0.15 wt% FS60) and 1.66 Pa s (0.075 wt% FS60) at elevated shear rates. These are the highest recorded values overall. However, the graph shows an increase of the dynamic viscosity values with increasing shear rate, followed by a slight decrease. It has to be assumed that coarse particles can settle during the measurement when the curve drops. The decreased concentration of particles over the main measuring surface may provoke this decrease in viscosity at high shear rates. In addition, the occurrence of structural rupture may be the reason for the decrease in viscosity at high shear rates. Wall slip could also occur. At low shear rates, the lowest values of 0.26 and 0.38 Pa s are attained. As the shear rate increases, the suspensions exhibit dilatant behaviour, accompanied by an increase in dynamic viscosity. Büchel *et al.*⁷ stated that increased resistance to flow and dilatancy can occur when refractory castables are pumped (which corresponds to high shear rates) if the matrix composition is not properly controlled. These

observations indicate that the interlocking of particles during material movement, which is a consequence of the coarse composition (with a low specific surface area), gives rise to dilatancy.

- The suspensions with a specific surface area of $2.7 \text{ m}^2/\text{g}$ exhibit comparable viscosity values of 0.25 and 0.40 Pa s at low shear rates and considerably lower values (than for $1.0 \text{ m}^2/\text{g}$) of 0.71 and 0.78 Pa s at higher shear rates. As the shear rate is increased, the curve approaches a Newtonian profile, which can be attributed to the specific surface area of $2.7 \text{ m}^2/\text{g}$, which is a multimodal composite mixture (Fig. 1). This phenomenon has been previously described in the literature on multimodal refractory castable matrices^{5, 6, 7, 8, 9}.
- The matrix mixture with the highest specific surface area of $4.7 \text{ m}^2/\text{g}$ exhibits a shear thinning curve at low shear rates. The initial dynamic viscosity values were recorded at 1.63 and 2.02 Pa s, respectively. The values are markedly higher than those of the other suspensions analysed, which can be attributed to the increased proportion of the finest component (reactive alumina with a specific surface area of $6.9 \text{ m}^2/\text{g}$). At higher shear rates, the values for both dispersing agent concentrations decline to 0.59 Pa s, which corresponds to a Newtonian range or weakly pronounced further shear thinning behaviour and represents the lowest viscosity observed among the measured suspensions in this series of experiments at high shear rates. This behaviour can be explained by the high specific surface area of the particles. In the resting state, numerous interparticle forces are built up, which lead to a high dynamic viscosity. Increasing shear reduces the interparticle adhesive forces, which leads to a decrease in dynamic viscosity⁹.

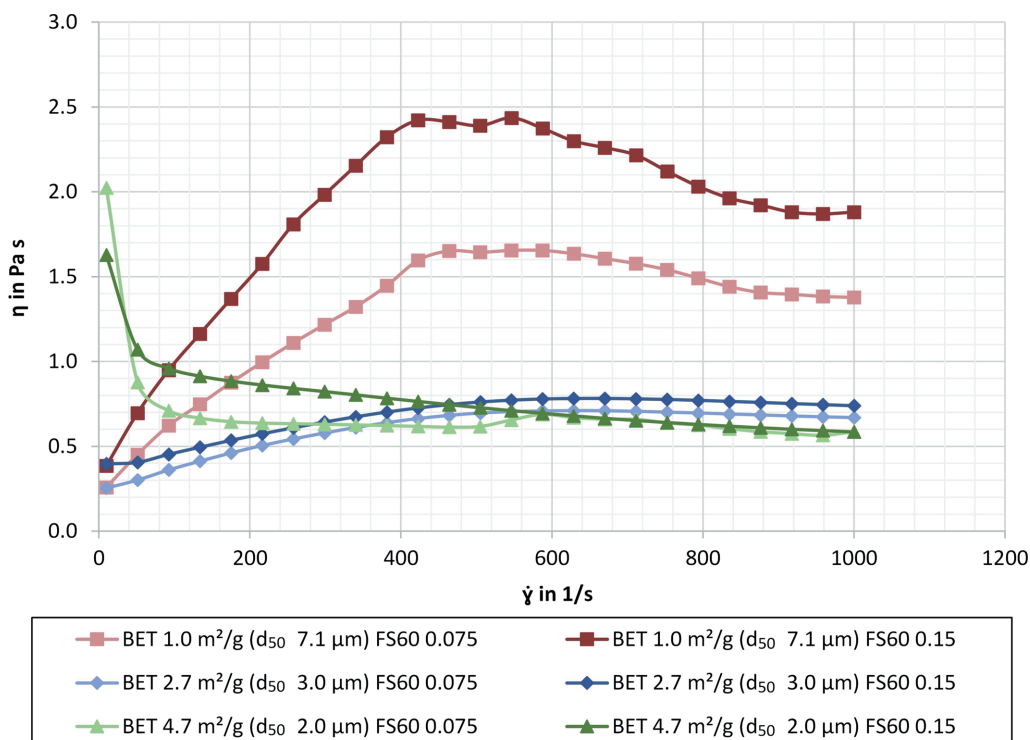


Fig. 3: Dynamic viscosities of the matrix suspensions shown in Table 4 and Table 5 with different specific surface areas and the PCE dispersing agent Castament FS60 in two different concentrations.

The general correlation that a higher concentration of dispersing agent leads to lower viscosity values cannot be observed, rather, the opposite appears to be the case. An entanglement of long-chain molecules (at higher concentrations), which leads to increased viscosity values, could also be considered.

PMA (Darvan 7S) and citric acid

The use of PMA (Darvan 7S in two different concentrations and with citric acid) leads to significantly lower overall values for the dynamic viscosity (Fig. 4) compared to the PCE dispersing agent Castament FS60 (Fig. 3). This can be attributed to the higher water requirement of castables, which is 6.3 wt% rather than 4.8 wt%. With PMA, a higher water content must be used due to a reduced dispersion strength in comparison to PCE. Despite a lower viscosity, the flow behaviour is worse. Here, the use of PCE leads to suspensions with a very low yield point in comparison to PMA (considering matrix suspensions 2.7 m²/g). In relative terms, however, the curves of the matrix suspensions dispersed with PCE and PMA exhibit comparable behaviour:

- The suspensions with a specific surface area of 1.0 m²/g display dilatant behaviour when the shear rate is increased. This is accompanied by an increase in dynamic viscosity, from 0.25 and 0.38 Pa s to 0.77 and 0.83 Pa s, before a slight decline (same explanation as for suspension 1.0 m²/g with PCE).
- With a surface area of 2.7 m²/g, the matrix suspensions display slight shear thinning behaviour at low

shear rates. Initially, viscosities of 0.27 and 0.58 Pa s are observed. As the shear rate is increased, the viscosity initially decreases to 0.18 and 0.32 Pa s before stabilizing at a low and Newtonian range of 0.28 and 0.34 Pa s, respectively (same explanation as for suspension 2.7 m²/g with PCE).

- As seen when the PCE dispersing agent system is used, shear thinning behaviour can be observed for suspensions with a surface area of 4.7 m²/g. However, these samples demonstrate the highest dynamic viscosities of the series, reaching 1.1 and 1.0 Pa s in the very low shear rate range. As the shear rate is increased, the values decrease and stabilize in the lowest and Newtonian range at 0.22 Pa s (same explanation as for suspension 4.7 m²/g with PCE). At this specific surface area of 4.7 m²/g and a Darvan 7S concentration of 0.07 wt%, stiffening occurs before the end of the measurement (marked with a dashed line in Fig. 4). For this reason, measured values after the stiffening time were not considered.

As with PCE, it appears that a higher dispersing agent concentration does not result in a reduction in viscosity. Instead, the respective curves are also in close proximity to or on par with one another, which is comparable within the dispersing agent change from PCE to PMA (neglecting the increase of water due to the reduced dispersion strength of the dispersing agent). In this case, this may be attributed to a less favourable ratio in relation to the

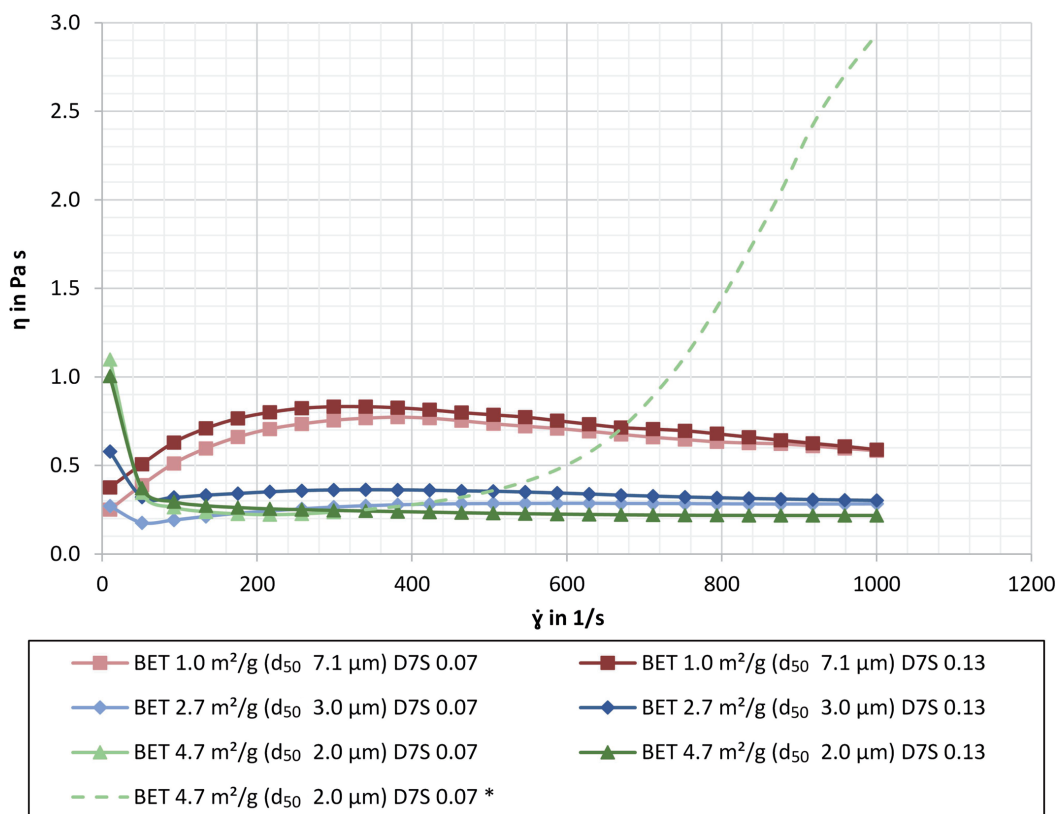


Fig. 4: Dynamic viscosities of the matrix suspensions shown in Table 4 and Table 5 with different specific surface areas and the PMA dispersing agent Darvan 7S (in combination with citric acid) in two different concentrations (*not considered part of the measurement due to stiffening is marked with a dashed line).

citric acid, which is maintained at a constant level. The influence of the uniform variation in the contents of PMA (Darvan 7S) and citric acid was investigated in this research environment, but has not yet been published.

S-TPP (N25 – 15) and citric acid

Fig. 5 shows that measurements of the dynamic viscosities with the use of S-TPP (N25 – 15 and two different concentrations of citric acid) resulted in lower values than those observed when utilizing PCE (Castament FS60) and PMA (Darvan 7S). This can be attributed to the higher water requirement for the castables of 6.7 wt% that was necessary due to the reduced dispersion strength by S-TPP and citric acid in comparison to PMA and PCE (Table 3):

- The matrix mixture with the lowest specific surface area ($1.0 \text{ m}^2/\text{g}$) exhibits a dilatant curve when the shear rate is increased. The initial values of 0.26 and 0.18 Pa s increase to 0.65 and 0.66 Pa s at higher shear rates, subsequently declining slightly (same explanation as for suspension $1.0 \text{ m}^2/\text{g}$ with PCE and PMA).
- As for PCE and PMA, the matrix suspensions with a specific surface of $2.7 \text{ m}^2/\text{g}$ demonstrate Newtonian behaviour (as it is a multimodal composite mixture (Fig. 1)) that is constant over the entire shear rate range. Average dynamic viscosities of 0.34 and 0.26 Pa s are observed for this suspension, respectively.
- The matrix suspensions with the highest specific surface area ($4.7 \text{ m}^2/\text{g}$) exhibited a shear thinning behaviour, with initial viscosities of 0.42 and 0.43 Pa s

decreasing to 0.18 and 0.17 Pa s, respectively (same explanation as for suspension $4.7 \text{ m}^2/\text{g}$ with PCE and PMA). A stable Newtonian curve was observed at higher shear rates and the lowest measured dynamic viscosities were recorded across all tests. With a reduced concentration of only 0.010 wt% citric acid, the matrix suspension exhibited a notable stiffening effect, comparable to that observed for the PMA system. However, because the stiffening started prior to the end of the measurement period the viscosity values subsequently increased (marked with a dashed line in Fig. 5). Therefore, measured values after the stiffening time were not considered.

For this dispersing agent system, it appears that a higher concentration of citric acid leads to lower viscosity values, which suggests that the flow behaviour can be specifically adjusted.

The results of the measurements of the dynamic viscosity of the matrix suspensions and various dispersing agent systems are employed to facilitate the interpretation of the other measurement methods. In the evaluation of the working properties, very small shear rates are considered by measuring the spreading dimension (slump flow) and the flow behaviour (by using a ball measurement system) of the real castables. The results of these investigations will be published in another article. Furthermore, high shear rate ranges are employed in the interpretation of the mixing energy required and the temperature development during mixing.

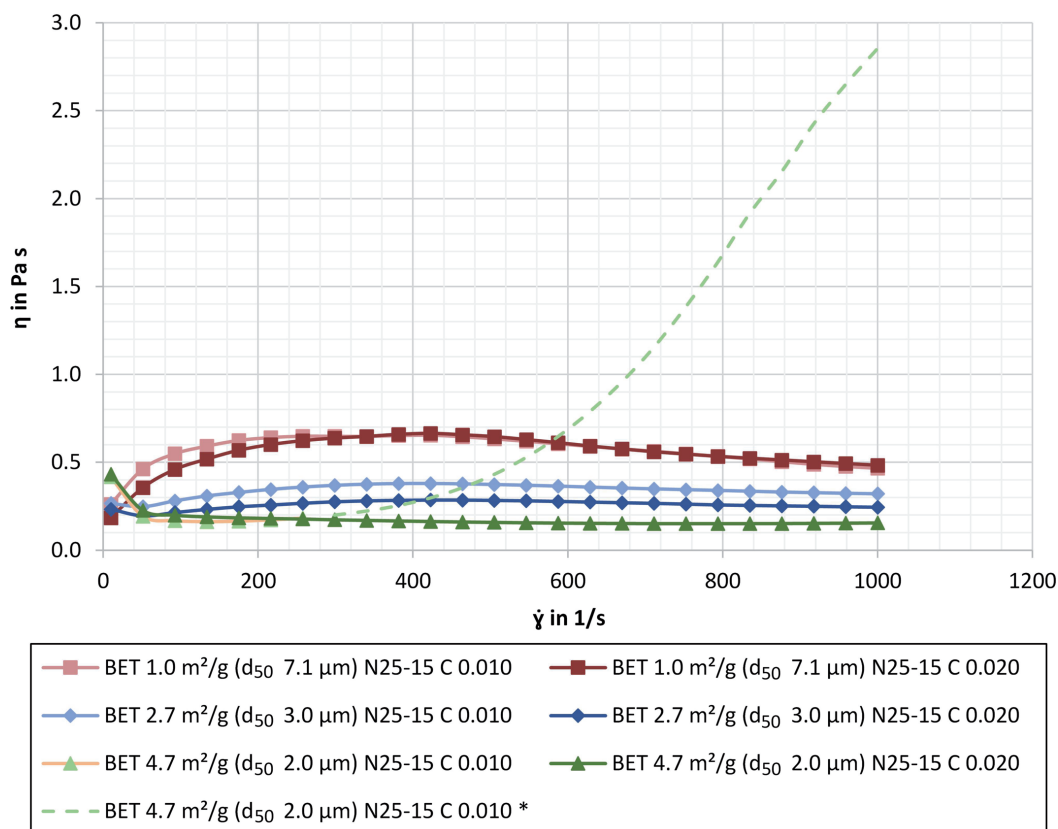


Fig. 5: Dynamic viscosities of the matrix suspensions shown in Table 4 and Table 5 with different specific surface areas and the S-TPP dispersing agent N25 – 15 in combination with citric acid in two different concentrations (*not considered part of the measurement due to stiffening is marked with a dashed line).

(2) Mixing energy during the mixing process

Fig. 6 depicts the evolution of the power consumption throughout the mixing process, as exemplified by the PCE dispersing agent Castament FS60 at a concentration of 0.10 wt% for the mixtures with varying specific surface areas (Table 2 and Table 3). The rise of the power consumption after 60 seconds correlates with the transition from dry to wet mixing following the addition of water. Due to initial agglomeration effects, the power consumption initially increases (before the dispersion mechanism becomes dominant) and, as described by Holleyn *et al.*²⁷, typically reaches a maximum, which corresponds to homogenization in the plastic state (in well-flowing refractory castables with multimodal distributed ceramic matrices and optimized properties). After that, power consumption can decline again due to the effect of finished dispersion and a deagglomeration of particles:

- For the mixture with a specific matrix surface area of 1.0 m²/g dispersed with PCE (Castament FS60 at a concentration of 0.10 wt%) a markedly dilatant behaviour is detected. The measured power consumption demonstrates a continuous increase up to a value of 1.15 kW at the end of the measurement (Fig. 6). This finding is affirmed by the results of the measurements of the dynamic viscosities of the corresponding matrix suspensions with a surface area of 1.0 m²/g, which also demonstrate dilatancy at high shear rates (Fig. 3). It can be concluded that the mixture with a surface area of 1.3 m²/g exhibits dilatant behaviour in an intermediate

period during the mixing process. However, following a maximum recorded energy of 1.29 kW and a mixing time of 240 s, a decline in the recorded power consumption is observed.

- The refractory castables with specific matrix surface areas of 2.7 and 3.0 m²/g reach maximum power consumption values of 0.80 and 0.82 kW, respectively, before exhibiting a rapid decline. The reduction in power consumption can be attributed to the particle size distribution. As previously outlined and also observed for the viscosities of the matrix suspensions, a bi- and multimodal particle size distribution results in a reduction of viscosity^{5, 6, 7, 8, 9}. The slightly lower maximum power consumption for the 2.7 m²/g mixture compared to 3.0 m²/g can be attributed to the multimodal particle size distribution (Table 2, Fig. 1 and Fig. 2).
- The lowest maximum values of the power consumption of 0.37 and 0.31 kW were observed for the mixes with the highest specific surface areas of 4.5 and 4.7 m²/g, respectively. Following a brief period of stability, the values decline once more. Both refractory castables display markedly reduced values of power consumption in comparison to castables with lower specific surface areas. Furthermore, the dynamic viscosities of the corresponding matrix suspensions in the high shear rate range also serve to reinforce these findings (Fig. 3). The flow behaviour (at high shear rates) can be described as almost Newtonian.

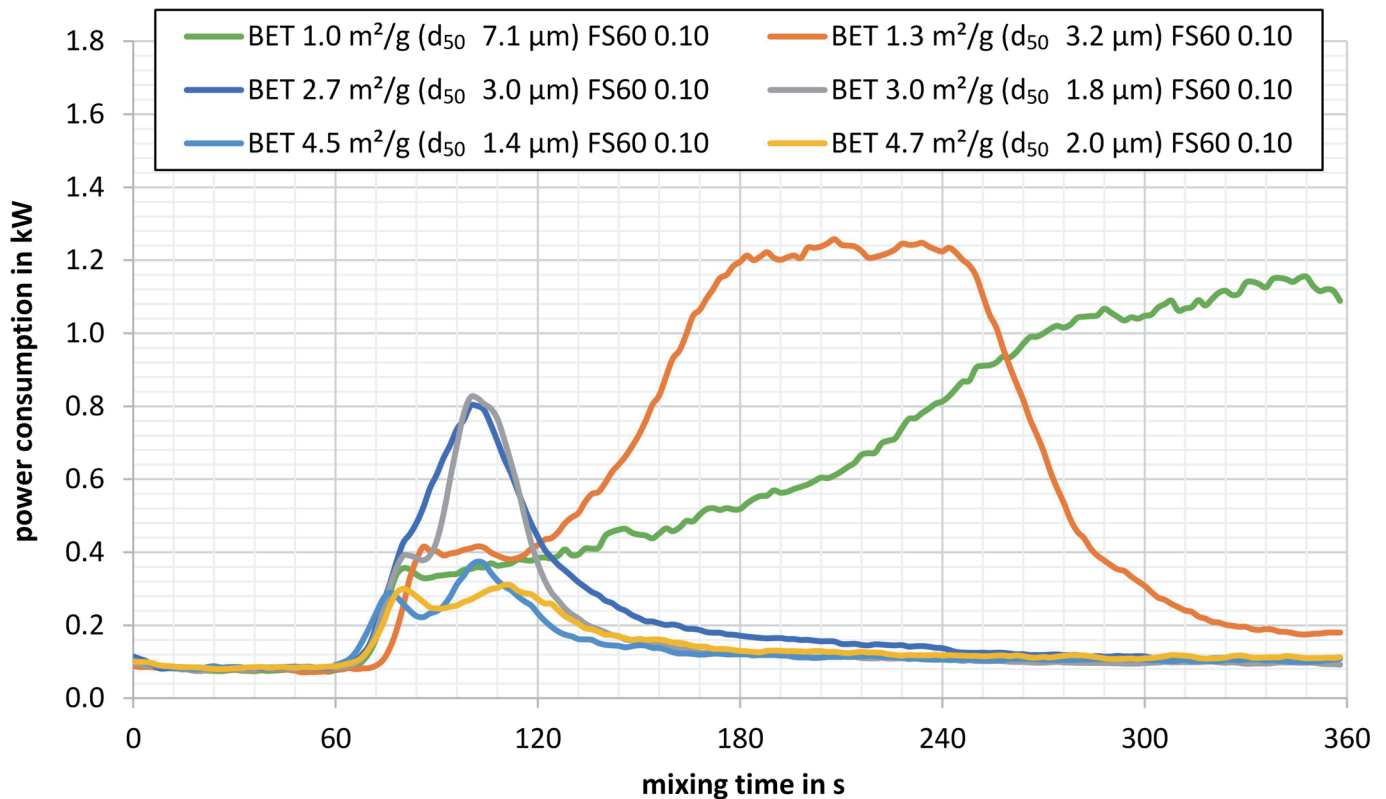


Fig. 6: Power consumption over the mixing time during the mixing process for the model castables with different specific surface areas using the example of the PCE dispersing agent Castament FS60 in a concentration of 0.10 wt% (Table 2 and Table 3).

In the PCE (Castament FS60) system a general trend can be recognized that matrix compositions with a high specific surface area show lower values of power consumption than castables with a low specific surface area. An evaluative conclusion from these results would be that shear thinning behaviour can be favoured during mixing, whereas dilatancy effects are energetically suboptimal and lead to increased wear of the mixing tool and an increase in temperature. Comparable results are observed when the power consumptions of all other mixes and dispersing agent systems PMA (Darvan 7S) and S-TPP (N25 – 15) and their different concentrations are considered. Nevertheless, the effects and differences in the recorded values of power consumption of PMA and S-TPP are less pronounced than in the mixtures with PCE. As observed with the corresponding matrix suspensions, this can be explained by the higher water content and the correspondingly lower viscosity at high shear rates.

For variations in the dispersing agent concentration, it can be observed that an increase results in a lower recorded maximum value of power consumption (Fig. 7). This was almost observed for all mixtures and dispersing agent systems and concentrations. However, it was not possible to work out the differences with the same precision as with PCE (Castament FS60), as the higher water contents (and thus lower values of power consumption) reduced the selectivity of the measurement results. The requirement of lower maximum values of power consumption can be attributed to the fact that a greater number of dispersing agent molecules are available per specific surface area, allowing them to adsorb onto the specific surfaces of the matrix particles. Therefore, the efficiency of the dis-

persing agent is enhanced, which facilitates the mixing of the refractory castable. Overdosing of dispersing agents was not considered and tested in this research work. However, it must be mentioned that potential overdosing can also have detrimental effects on the flow behaviour of all types of polymer additives.

In order to facilitate a more accurate comparison of the various model castables, the required mixing energy over the respective total mixing time was calculated based on numerical integration of the measured power consumption. The total mixing energy required for the refractory castables (Table 2 and Table 3) is shown in Fig. 8. The mixing energy for the mixes with PMA (Darvan 7S) and S-TPP (N25 – 15) exhibit less variation with regard to the dispersing agent concentration and are significantly lower than for the mixes with PCE (Castament FS60). This can be attributed to the higher water contents of 6.3 and 6.7 wt% (for PMA and S-TPP) to 4.8 wt% (for PCE), as observed in the matrix suspensions. Higher water contents lead to a reduction in the interparticle forces at the high shear rates of mixing. A notable trend emerges when the considered dispersing agent systems are examined: Castables with lower specific surface areas of the matrix necessitate more mixing energy than those with higher surface areas. A lower specific surface area results in dilatancy effects due to higher internal friction, which is why more energy is required. The utilization of a higher dispersing agent concentration results in a reduction in the required mixing energy. The effect of potential overdosing of dispersing agents was not part of this research and was not investigated.

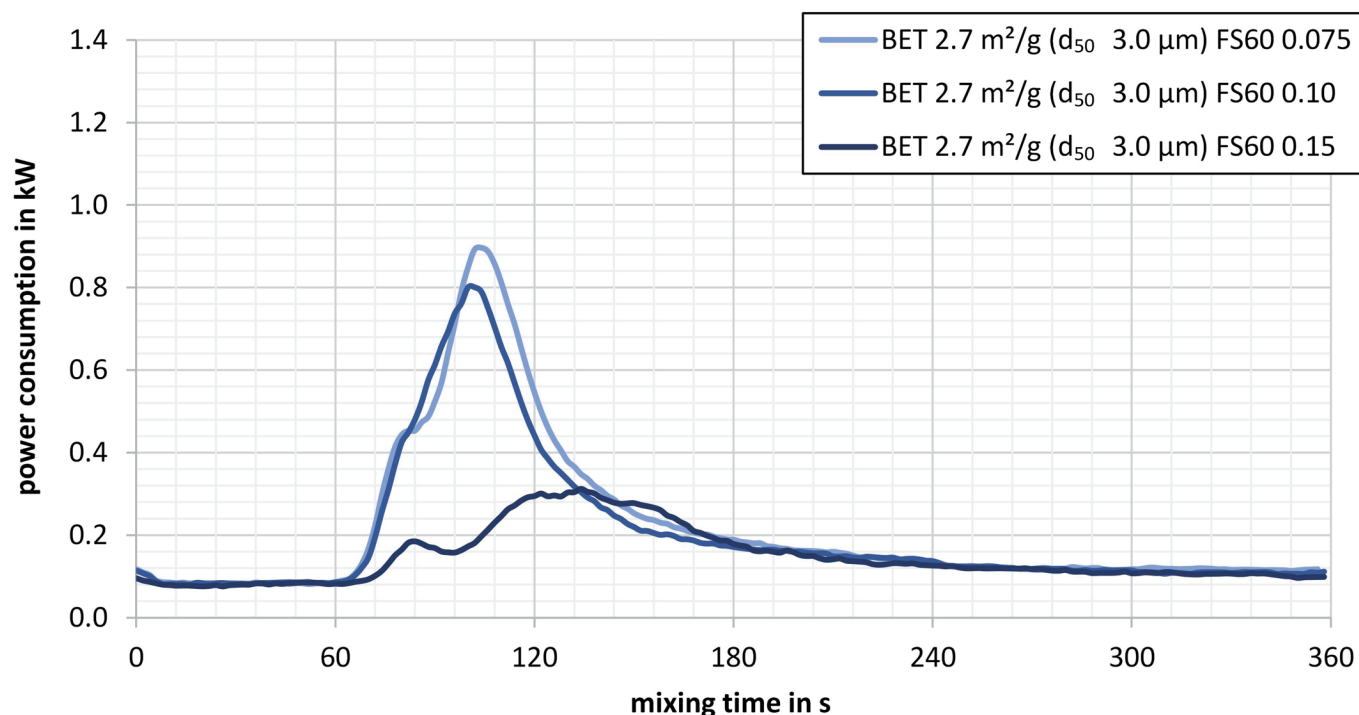


Fig. 7: Power consumption over the mixing time of model castables with a specific surface area of $2.7 \text{ m}^2/\text{g}$ with concentrations of the PCE dispersing agent Castament FS60 of 0.075, 0.10 and 0.15 wt% (Table 2 and Table 3).

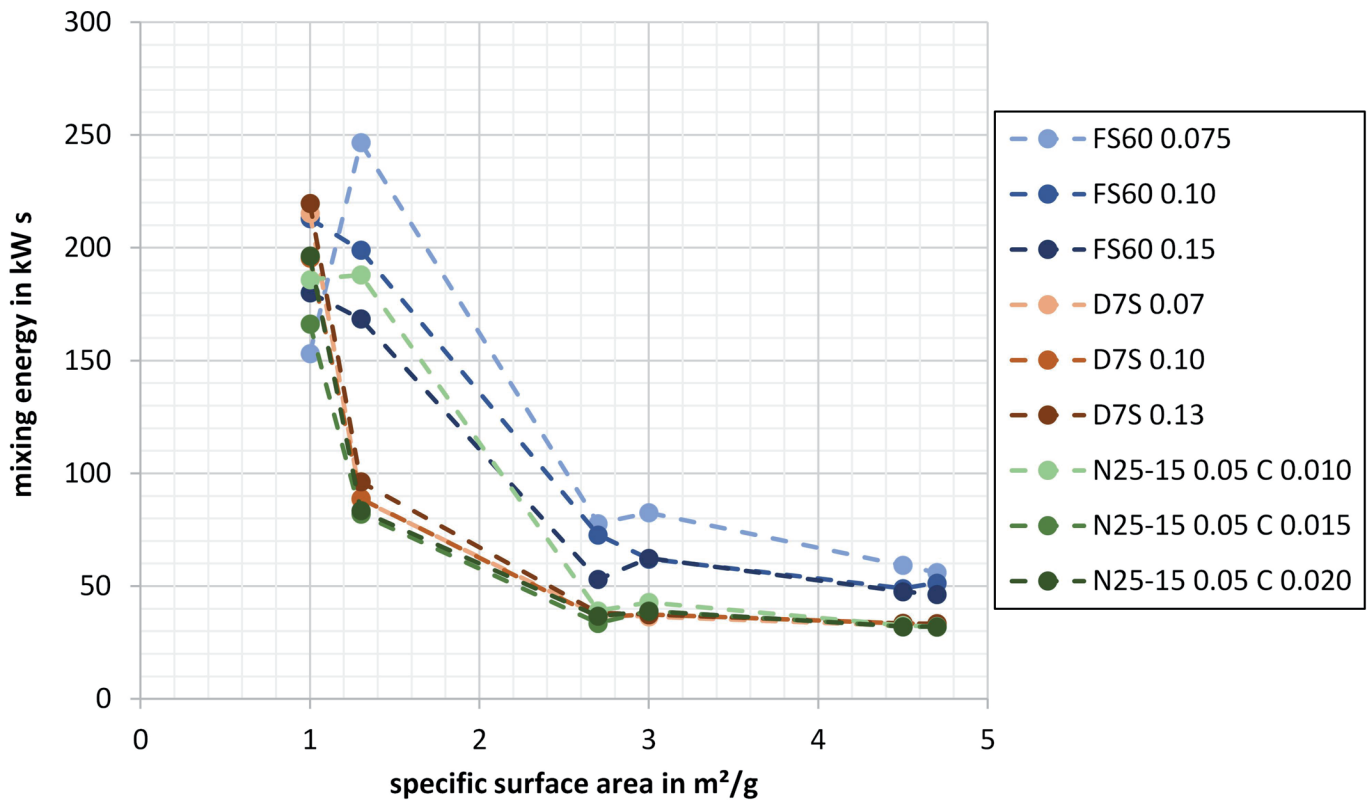


Fig. 8: Mixing energy of all refractory model castables considered with different specific surface areas and dispersing agents and concentrations (Table 2 and Table 3).

The value for the mixing energy for the refractory castable with a surface area of 1.0 m²/g and the concentration of Castament FS60 of 0.075 wt% does not align with the established pattern. However, it is essential to exercise caution when interpreting this result. The lowest concentration of Castament FS60 and the highly dilatant behaviour of this refractory castable may have resulted in an input of very high mixing energy, potentially leading to an overload of the belt-driven mixer drive resulting in slipping of the drive V-belts. This could lead to low recorded values, as the agitator can no longer rotate as controlled.

The slightly elevated mixing energy required by mixtures 3.0 m²/g, in comparison to 2.7 m²/g, does not align with the aforementioned trend that refractory castables with a higher specific surface area of the matrix demand less mixing energy than those with lower surface areas. It is necessary to discuss the particle size distribution of the matrix. Measurements of the dynamic viscosity of suspensions with a specific surface area of 3.0 m²/g demonstrated dilatancy effects within the high shear rate range. One explanation for the dilatancy effects that occur (although weakly pronounced) could be the high proportion of a single particle fraction (19 wt% of CTC20) in this matrix composition despite a higher specific surface area (Table 2 and Fig. 2). Due to the high proportion of only one fine particle fraction, the shearing can lead to increased collision of the particles, which leads to an increase in viscosity and dilatancy effects (even with small particles)⁹. In contrast, mixture 2.7 m²/g has a multimodal distribution of fine particles, which could have a positive influence on the

mixing energy^{5, 6, 7, 8, 9}. However, these assumptions still need to be verified in further tests.

(3) Temperature evolution during the mixing process

Measurements of the temperature during the mixing process showed that the temperature evolution during the process is directly correlated with the mixing energy, and consequently, with the specific surface area of the matrix (Fig. 8 and Fig. 9). It is becoming increasingly evident that mixtures with matrices containing larger quantities of highly sintered and (very) finely ground alumina raw materials (with high specific surface areas) undergo a less pronounced heating during the mixing process than castables with lower specific surface areas. A dashed line in Fig. 9 describes the dependence of mixing energy and temperature evolution (with a degressive progression). The application of PCE resulted in temperature increases of the refractory castables with varying surface areas, ranging from 3.1 to 13.3 °C, during the mixing process. The castables dispersed with PMA and S-TPP exhibit reduced mixing energies (Fig. 8). This provides an explanation as to why these systems typically result in slightly reduced heating, particularly with finely composed refractory castables, at a range of 1.0 to 13.0 °C and 0.8 to 13.3 °C, respectively. The higher water demand of PMA and S-TPP compared to PCE (which leads to lower required mixing energies) plays a role here. With PMA and S-TPP, a higher water content must be used due to a reduced dispersion strength in comparison to PCE.

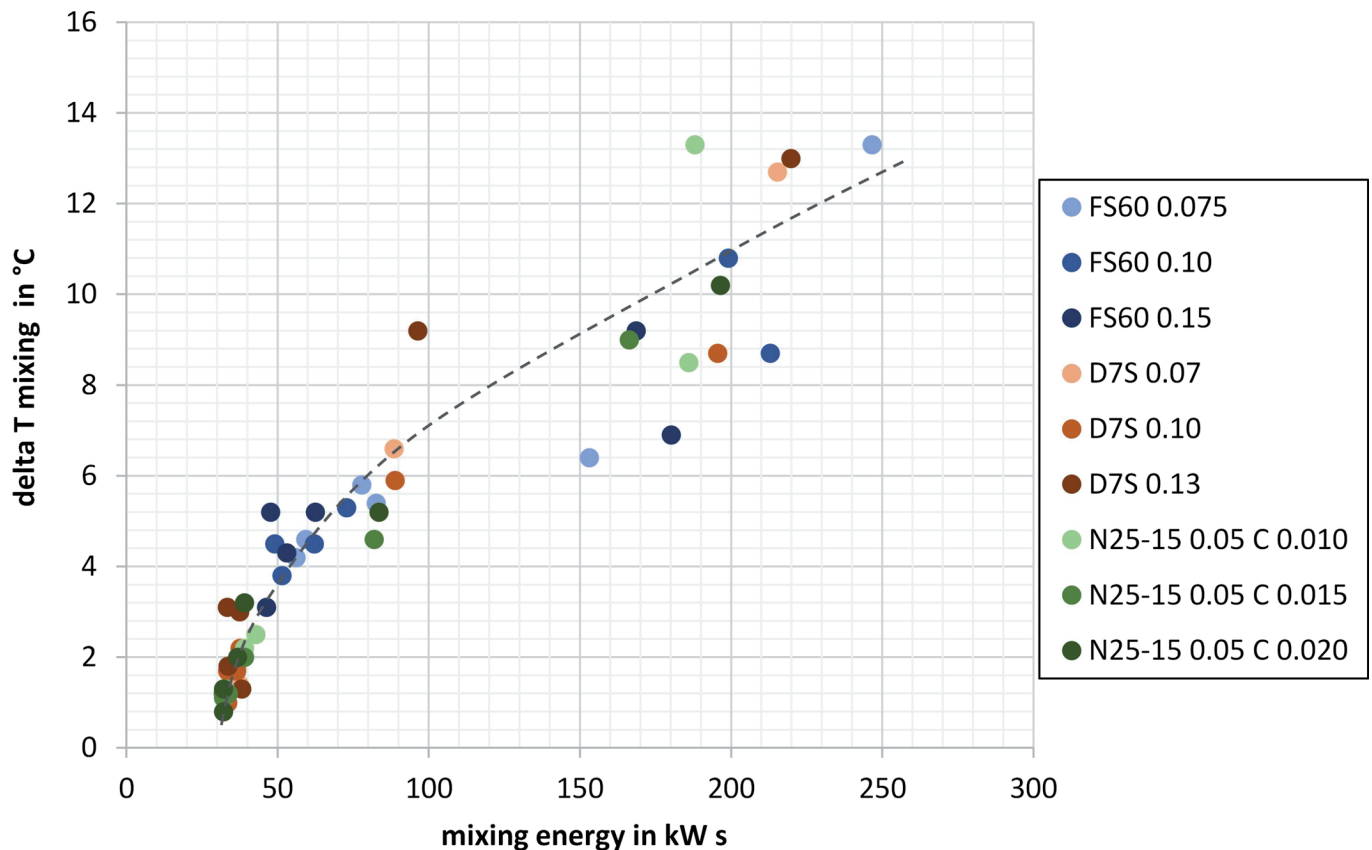


Fig. 9: Visualization of the direct dependence of the required mixing energy and the temperature increase during the mixing process of all considered model castables with different specific surface areas and dispersing agents and concentrations (Table 2 and Table 3).

IV. Conclusions

This study presents the systematic investigation of six developed self-flowing, high-alumina, CA-cement containing refractory model castables with a maximum particle size of 6 mm. The matrix (particles $\leq 45 \mu\text{m}$) was modified by means of targeted alteration of the particle size distribution and therefore the specific surface area (by using highly sintered and (very) finely ground alumina raw materials with high specific surface areas) to investigate the impact on dispersion and mixing energy. In addition, three different dispersing agents and their concentrations were systematically varied for this purpose. The effect of potential overdosing of dispersing agents was not part of this research and was not investigated.

The dynamic viscosities of the matrix suspensions for the dispersing agents Castament FS60 (PCE), Darvan 7S (PMA) with citric acid and N25–15 (S-TPP) with citric acid are dependent on the specific surface area, dispersing agent, concentration and shear rate. Suspensions with low specific surface areas of the matrix ($1.0 \text{ m}^2/\text{g}$) display dilatant behaviour and higher dynamic viscosities when the shear rates are increased. In contrast, suspensions $2.7 \text{ m}^2/\text{g}$ tend to exhibit Newtonian behaviour over the entire shear rate range, which can be attributed to their multimodal matrix composition. Suspensions with a high surface area ($4.7 \text{ m}^2/\text{g}$) exhibit high viscosities (at low shear rates) and a shear thinning behaviour. However, when the shear rate is increased, there is a notable decline in dynamic viscosity, accompanied by the observation of Newtonian flow.

Comparisons between dispersing agents show that PMA and S-TPP have lower viscosities than PCE, whereby the higher water requirement plays a central role. With PMA and S-TPP, a higher water content must be used due to a reduced dispersion strength in comparison to PCE. Despite a lower viscosity, the flow behaviour of the respective refractory castables (controlled by slump-flow, which corresponds to very low shear rates) is worse. Suspensions with higher specific surface areas of the matrix tend to exhibit lower viscosity values at elevated shear rates, irrespective of the dispersing agent employed.

It can be observed that refractory castables with a high specific surface area of the matrix (independent of the dispersing agent systems under consideration) require less mixing energy than those with a lower specific surface area. Castables with a low specific surface area (1.0 and $1.3 \text{ m}^2/\text{g}$) require the highest mixing energy, indicating highly dilatant behaviour at the high shear rate during mixing. In contrast, mixes with higher specific surface areas (2.7 , 3.0 , 4.5 and $4.7 \text{ m}^2/\text{g}$) require significantly less energy. The application of higher dispersing agent concentrations has been observed to reduce the mixing energy, which can be attributed to the increased availability of dispersing agent molecules for adsorption onto particle surfaces, thereby enhancing the efficiency of the dispersion process. The differences are less evident when PMA and S-TPP are employed (instead of PCE), as the elevated water content enhances the mixing process. These findings are consistent with observations made when measuring the dynamic viscosity of matrix suspensions in the high

shear rate range. A direct correlation between the temperature increase during the mixing process of all model castables with different specific surface areas and dispersing agents and concentrations and the required mixing energy can be clearly established. It can be observed that mixtures with matrix compositions exhibiting a higher specific surface area and also those with a higher dispersing agent concentration undergo a lower degree of heating during the mixing process than castables with lower specific surface areas.

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